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UNIVERSITY OF ALBERTA

A RECONNAISSANCE STUDY OF SOME WESTERN
CANADIAN LEAD-ZINC DEPOSITS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF GEOLOGY

by

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April, 1965

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "A Reconnaissance Study of Some Western Canadian Lead-Zinc Deposits", submitted by Thomas L. Evans, B.Sc., in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

A number of lead-zinc deposits occur in the southeastern Canadian Rocky Mountains in the Banff-Lake Louise, Alberta and Field, British Columbia areas, and in the Liard Basin of Western Canada. The deposits occur in Cambro-Ordovician strata in the mountains and Devonian strata in the Liard Basin. The deposits occur in carbonate or argillaceous rocks, and have been classified as Mississippi Valley Type low temperature deposits.

Twenty representative sphalerites were analyzed by X-ray fluorescence techniques for iron, cadmium, manganese and selenium and 12 galenas were analyzed for selenium. Cell edge measurements were made on 15 sphalerites and these compared to the cell edge calculated from the amounts of iron, cadmium and manganese in each sphalerite. The chemical analyses and cell edge determinations yielded results similar to other published values for similar sphalerites.

The sulfur isotope ratios of 31 sulfide minerals (sphalerite, galena, chalcopyrite and pyrite) were determined by mass spectrometric analysis. All the samples were found to be enriched in the heavier isotope (S^{34}) and the δS^{34} values ranged from +8.1 to +31.3 mils.

The writer believes the sulfur originated from the source rocks by some biogenic or other process. Since there is no obvious igneous source, the writer believes that the metals came in with hydrothermal solutions mobilized by a heat source of unknown origin. These solutions were probably connate waters or a mixture of connate and dilute magmatic waters.

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INTRODUCTION

General Statement

Lead-zinc deposits of the Mississippi Valley Type described by Ohle (1959) occur in many places in the world and are of great economic importance. In Canada the recent development of the huge Pine Point deposit has brought attention to this type of deposit. There are, however, a number of smaller deposits of this general type found in the eastern section of the Canadian Rocky Mountains. Although most of these deposits are located within the boundaries of several National Parks and cannot be developed, they merit study as they pose an interesting problem of genesis.

The theme of this thesis is a reconnaissance comparative study of several of these deposits from the viewpoint of their mineralogy, geochemistry, and sulfur isotope abundances. The use of the mineralogy and geochemistry of an ore deposit has always been a very useful tool in studying ore genesis, but since the pioneer work by Thode and his co-workers (1949), the application of studying variations in isotopic abundances of the stable isotopes of sulfur (S^{32} and S^{34}) have become more and more important in determining the origin of many types of deposits.

Bearing in mind the usefulness of these research procedures the results of this study have been used to infer an origin for some of the Mississippi Valley Type lead-zinc deposits found in Western Canada.

Location and Accessibility

Sulfide deposits at the Monarch-Kicking Horse Mines, Hawk Creek, Baker Creek, and Eldon showings are located in eastern British Columbia and western Alberta, within the South Central Canadian Rockies. Other sulfide minerals investigated are from the Pine Point mine located on the south shore of Great Slave Lake, N.W.T., and from the Pan American, Beaver River A-1 well located at lat. $59^{\circ} 58' 12''$ N long. $124^{\circ} 17' 12''$ W (Figure 1) in northeast British Columbia. (See map in pocket for locations of Rocky Mountain deposits).

The Kicking Horse and Monarch deposits are three miles east, on the Trans-Canada Highway, from Field, British Columbia, in the Yoho National Park. The Kicking Horse deposits are on Mt. Field, and the Monarch deposits are on Mt. Stephen. The lead and zinc sulfides are distributed over the steep talus slope below the lower portals of Kicking Horse Mine. The Monarch mine workings are inaccessible without proper climbing equipment.

The Hawk Creek deposit is in Kootenay National Park on the north side of Hawk Creek, two miles east of the Banff-Radium Highway. The deposit may be reached by turning east at the Highway Department road camp located 4 1/2 miles north of Vermilion Crossing. The first half mile may be driven to the camp water supply area on Hawk Creek. At this point a trail begins on the north side of Hawk Creek and continues 1 1/2 miles to within 200 feet of the main showing.

The Eldon Mine is located 1.3 miles west of the Banff-Lake Louise section of the Trans-Canada Highway. The mine is located on the east flank of Panorama Ridge and may be reached by means of a horse trail leaving the highway at a point 25.4 miles northeast of Banff, Alberta.

The Baker Creek claims are located on the east side of the Bow Valley opposite the Eldon mine. These too may be reached by a horse trail leaving Highway No. 1, alternate, at a point 25.9 miles northwest of Banff. Both the Eldon mine and Baker Creek horse trails are marked by blazed trees that lead to the showing.

General Geology

The Monarch, Kicking Horse, Hawk Creek, Eldon mineral deposits, and the Baker Creek claims lie within the Main Range Sub-Province of the Rocky Mountain System. A further division places the deposits in the Eastern Ranges of the Main Range Sub-Province (North and Henderson, 1954). The area is characterized by high, rugged mountains and deeply glaciated valleys. The rocks are mostly lower Paleozoic in age. The present topography is the result of extreme

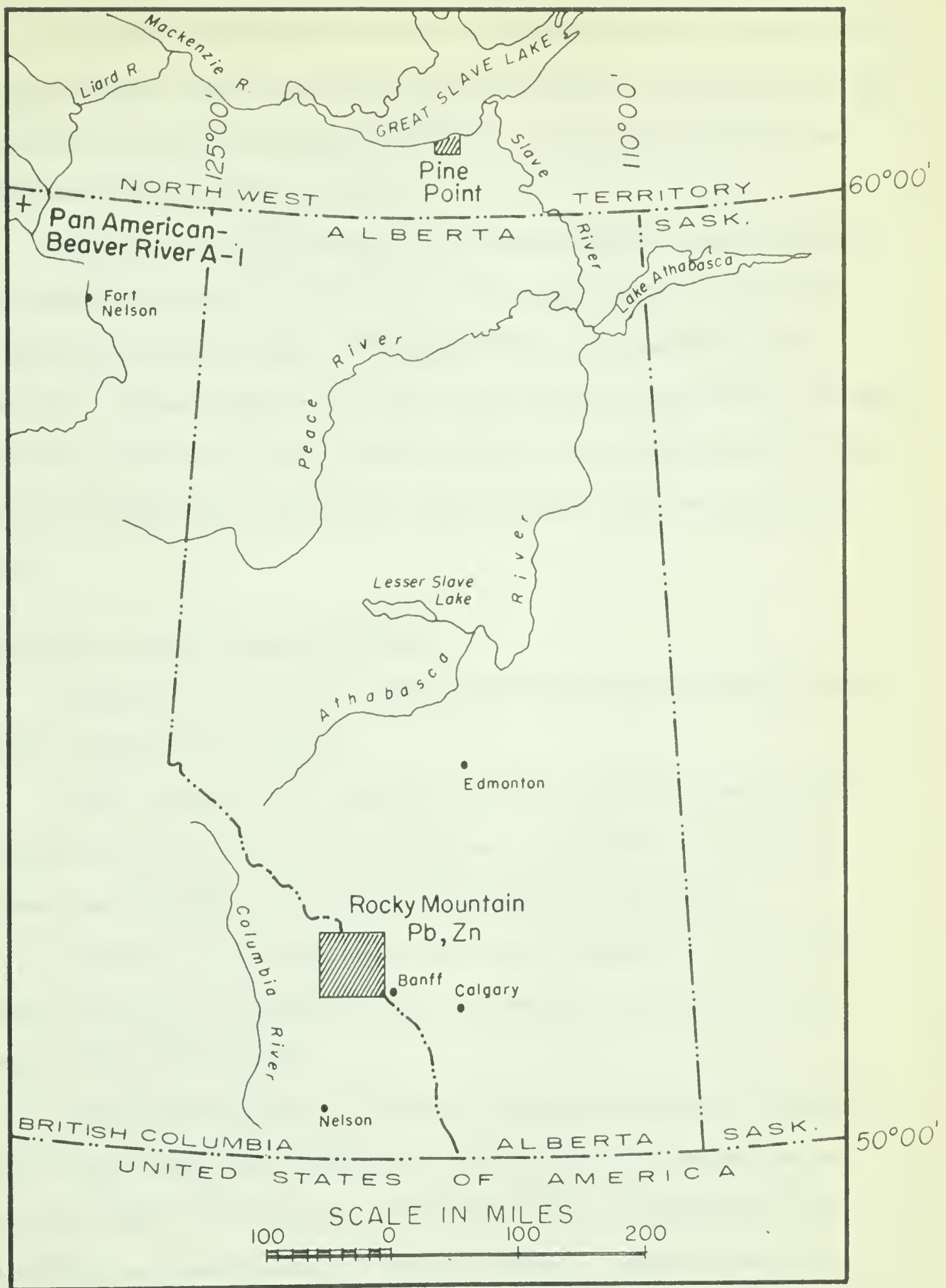


Figure 1. Location Map.

mountain building processes involving intense folding and faulting followed by erosion. The present attitudes of the strata are probably the result of several periods of crustal movement beginning during the Devonian (350 M.Y. ago) and occurring intermittently through the Cretaceous (100 M.Y.). The mountain building events culminated with the Laramide Revolution.

The rocks of the Main Ranges of the Canadian Rockies range in age from late Precambrian through Lower Ordovician. The mineral deposits occur in the rock formations of Lower, Middle, and Upper Cambrian and possibly in Lower Ordovician. The ore bodies of the Kicking Horse-Monarch deposits are in limestone and dolomite. The Hawk Creek ore body is in limestone and argillite and the Eldon deposit is in similar shaly, argillaceous, black limestone which has been highly sheared.

Similar Ore Deposits Throughout the World

Lindgren (1932) proposed a depth zone classification for lead-zinc sulfide deposits. The three main types are:

1. High Temperature - The sphalerites contain up to 39 mole percent FeS in solid solution with ZnS. The lead-zinc ores may be associated with sulfosalts, antimony bearing sulfides. The Sullivan Mine deposit is of this type.
2. Moderate to Low Temperature - This type is often high in silver content and may have barite as a gangue mineral. The deposit at Torbrit, B.C. is an example of this type of deposit.
3. Mississippi Valley Type - These are near surface deposits not thought to extend to great depths; their deposition having taken place at temperatures not greater than 200°C. This type is usually found as massive replacements, open space fillings and disseminations in limestone, dolomite, argillites, and other clastic sediments. These have been called "telemagmatic" or "telethermal". Some of the telethermal deposits are listed in Table 1.

TABLE 1
SOME MISSISSIPPI VALLEY TYPE Pb-Zn DEPOSITS

<u>Country</u>	<u>Location</u>	<u>Type of Minerals</u>
Canada	Pine Point, N.W.T.	Lead-Zinc
	Canadian Rocky Mountains	Lead-Zinc-Copper
U.S.A.	Southwest Missouri	Lead-Zinc
	Tri-State, Mo., Kan., Okla.	Lead-Zinc
	East Tennessee	Zinc
	Upper Mississippi Valley	Lead-Zinc
Poland	Upper Silesia	Lead-Zinc
Sweden	Laisvall	Lead-Zinc
Germany	Mechernich	Lead
Rhodesia	Broken Hill	Lead-Zinc

Dunham (1948) has sub-divided the telethermal deposits into three types:

1. Disseminations and massive replacements in limestone and dolomite in regions of flat-lying or gently folded sediments, related to minor faults, flexures, or joints as in the Mississippi Valley of the United States and Upper Silesia of Poland.
2. Disseminations and massive replacements of limestone and dolomite in regions of strong folding and overthrusting; as is the case in East Tennessee, and the Carinthian Alps. The Canadian Rocky Mountain deposits fall into this category.
3. Disseminations in sandstone such as the "Red Bed" deposits of Mechernich, Germany.

Since ore deposits of the telethermal type have produced vast quantities of lead and zinc, and the Canadian telethermal lead-zinc deposits considered in

this study are similar to other Mississippi Valley types, a brief discussion of a few of these deposits follows below.

Tri-State District

The Tri-State District takes in an area 125 miles long and 52 miles wide and covers portions of Missouri, Oklahoma, and Kansas. The deposits of this region, the leading producing area of the United States, occur in limestone and chert of the Boone Formation and locally in the overlying limestones and sandstones of the Chester Group. All of the rocks mentioned are of the Mississippian Age. Evidence indicates that the Boone limestones were attacked by groundwater solution prior to Chester time and again in Post-Pennsylvanian time, forming circulation channels and sink holes.

The strata are mainly flat-lying but minor synclinal and anticlinal folds trend N.E. and N.W. Zones of crushing and brecciation have played a major role in the deposition of the lead and zinc sulfide deposits. The gangue and ore minerals replace the limestone of the favourable beds or fill fractures in the brecciated chert.

Southeast Missouri District

The southeast Missouri deposits occur in a belt extending 35 miles long and 3 to 5 miles wide in a northwesterly direction in Francois and Madison Counties. The deposits usually occur in the lower part of the Bonneterre dolomite of Late Cambrian Age. The Bonneterre Formation is underlain by a thick sandstone unit lying on top of buried Precambrian hills of granite and rhyolite porphyry.

The ore bearing strata are almost horizontal but gentle undulation usually occur above the buried Precambrian hills. Locally, ore deposits may encircle these hills in the dolomitic units. Disseminated galena is the most important ore mineral but large crystals of galena and sphalerite in vuggy dolomite constitute a considerable portion of the ore. These minerals occur as massive replacements, vein fillings

and cavity fillings where solution channels and holes have been formed by traversing groundwaters.

Kentucky-Illinois District

The fluorite, sphalerite, and galena deposits of this region occur as veins in faults that cut Mississippian limestones and as tabular bedding replacement deposits in the Mississippian limestones.

The deposits are in nearly flat-lying strata on the flank of a faulted dome. The primary ore and gangue minerals are fluorite, sphalerite, galena, chalcopryite, marcasite, pyrite, calcite, quartz, and barite.

Upper Mississippi Valley District

These ores occur in the Galena Dolomite and Upper Platteville Formation, all of Middle Ordovician Age. This area lies in a region of folding, faulting, and fracturing. Behre et al. (1948) state that regional and local structural features controlling the ore bodies appear to have been formed by regional tectonic stresses. They state 80 percent of the ore bodies conform to these structural trends.

Primary minerals include galena, sphalerite, chalcopryite, millerite, and a host of gangue minerals. On the whole the structural features, the more diverse mineralogy, and a wider range of trace elements, tend to set this district apart from the more typical Mississippi Valley Type of deposit.

Upper Silesia, Poland

Zwierzycki (1948) reports that the Upper Silesia lead-zinc deposits occur in the Muschelkalk beds which are shallow water marine sediments of Jurassic Age. The rocks were mildly folded and faulted during the Lower Jurassic and the Muschelkalk has been preserved in several synclines and troughs trending in a northwesterly direction.

Ore deposition was preceded by extensive dolomitization; two ore-bearing

beds, the Lower and Upper Wavy Limestones were particularly susceptible to dolomitization. The primary minerals include sphalerite, wurtzite, galena, pyrite, marcasite, and jordanite, gratonite (lead arsenic sulfide) and meneghinite (lead antimony sulfide). The principal ore horizons usually occur at the base of the dolomite zones, a feature common to the Kicking Horse-Monarch mines of eastern British Columbia.

GENERAL GEOLOGY OF THE DEPOSITS

The amount of information available on the geology of these deposits is very limited, with the exception of the Monarch-Kicking Horse deposits located near Field, British Columbia. Past work in the Field area consists of an early report by Allan (1914), and reports by Goranson (1937); Brown (1948); and Ney (1954). Dawson (1885) reports quartz veins containing chalcopyrite near the summit of Copper Mountain, the veins trend in a north south direction and are usually found near a quartzite-limestone contact. In places throughout the mineralized zone the primary chalcopyrite has been oxidized and redeposited as azurite $[\text{Cu}_3 (\text{CO}_3)_2 (\text{OH})_2]$ and malachite $[\text{Cu}_2 \text{CO}_3 (\text{OH})_2]$. At that time Dawson considered this Rocky Mountain region to be a future metal producing area despite the fact that the ore seemed to occur as irregular, but rich, pods and gash veins rather than large massive bodies. As far as could be determined there have been no formal reports written on the Eldon or Baker Creek deposits which were presumably explored in the 1890's or early 1900's. These have been forgotten about since Banff National Park was created. The Hawk Creek deposit was discovered in 1929 and evaluation work was done in 1942 under the supervision of the federal government. Henderson (1953) produced the only report on the deposit in which he gives the results of the surface trenching and diamond drilling carried out during this program. A brief account of the geological features in the Pine Point area is given by Campbell (1952).

Kicking Horse and Monarch Mines

The sedimentary rocks in the vicinity of the mines are all Cambrian in age. The stratigraphic succession on Mt. Stephen, where the Monarch Mine is located, consists of Lower Cambrian St. Piran quartzites, followed by the Middle Cambrian shaly limestones of the Mount Whyte and the Cathedral Formations, consisting of dark grey to light grey limestone, which is in part dolomitized. The mines are located within the dolomitized unit of the Cathedral. The blocks of dolomitized Cathedral

on Mt. Field and Mt. Stephen are bounded on the west and east by two large normal faults known as Stephen-Field and Stephen-Cathedral faults respectively. Ney (1954) reports the ore bodies are flattened, oval-shaped pods. The Monarch ore bodies extends southeast into Mt. Stephen for distances up to 2400 feet. The Kicking Horse ore bodies extend into Mt. Field for distances up to 2400 feet.

The mineralization consists of galena, sphalerite, and pyrite. The ore bodies always occur in brecciated dolomite of two general types. One type is grey with a light crystalline dolomite matrix, the other is a white breccia consisting of numerous coarse, white, dolomite veinlets in grey dolomite. The ore minerals in places replace grey breccia. The sulfides show a preference for the matrix, but in some samples the breccia fragments may be completely replaced by ore. Horizontal bands one foot or more thick of almost pure lead and zinc sulfide occurs sporadically, especially near the footwall of the ore body (Ney, 1954). The carbonate present in the immediate vicinity of the mines is usually white, coarsely-crystalline dolomite whereas most of the dolomite found throughout this part of the Rocky Mountains is fine-grained and fairly well-bedded. The coarsely crystalline variety is probably related directly to the ore deposits and may have been formed by the hydrothermal event that formed the deposits. One interesting aspect is the localization of the ore near the base of the dolomite adjacent to the dolomite-limestone contact. The ore shoots in places extend several feet into the underlying black limestone but this is not common. Ney (1954) emphasizes the presence of dolomitized alteration halos around the ore zones.

Hawk Creek Deposit

The area in the vicinity of these showings is underlain by a series of inter-bedded grey limestones and brownish-grey argillites of probable Upper Cambrian or Ordovician Age. At the sulfide mineral exposures, the beds are almost horizontal and are cut by a northwest-trending shear zone dipping 45 to 70 degrees to the

southwest. Henderson (1953) believes the shear zone might extend well beyond the known limits of mineralization.

Henderson reports the ore zone consists mainly of massive sphalerite replacing limestone. The sulfide mineralization is localized at the intersection of the shear zone and a favourable limestone horizon. This association suggests a combined structural and lithologic control during ore deposition. Diamond drill data indicate a cigar-shaped ore pod about 250 feet long, 55 feet wide and 18 feet high. Henderson has estimated that a total of 29,500 tons of ore grade material, averaging 12.5 percent zinc, occurs in this pod.

The deposit contains two types of sphalerite. The dominant variety is a light brown sphalerite that occurs as massive or disseminated aggregates replacing limestone. The other type is a dark reddish-brown variety seen only as disseminations in or near veins and patches of white crystalline dolomite. Galena occurs as replacement bands, and appears to be associated in a general way with the reddish-brown sphalerite and white dolomite (See Plate II and III for photomicrographs of the ore minerals). Pyrite occurs in minor quantities as fine grains disseminated throughout the ore although certain bands, less than 1 cm wide may contain considerable pyrite.

Eldon Deposit

The Eldon copper-lead-zinc deposit is situated in brown, calcareous and argillaceous rocks of probable Lower or Middle Cambrian Age. These rocks are cut by an east-trending shear zone that dips about 40 degrees north.

The mine entrance has caved, therefore access to the workings is not possible. Judging by the amount of material present on the dump, the adit may have extended several hundred feet back into the mountainside. The material found in the mine dump indicates that the deposit consisted of sphalerite, chalcopyrite, galena and minor pyrite in gangue material of quartz and siderite. This deposit is unique with respect to the other Rocky Mountain deposits considered in this study

since it has abundant quartz, siderite, and chalcopyrite as constituents. Minor amounts of sercite was noted intimately associated with the sulfide minerals.

The presence of vein quartz indicates that the deposit appears to have some characteristics of a true vein deposit. Minor quartz veinlets were observed in all the argillaceous sediments in the immediate vicinity of the zone of mineralization.

Baker Creek Claims

These prospects, located on the extreme northwest flank of Mt. Eisenhower, occur in black dolomite veined with white, crystalline, coarse-grained dolomite. The rocks are probably Middle Cambrian in age and may belong to the Cathedral Formation, which is present in thicknesses of up to 1000 feet on Mt. Eisenhower (North et al. 1954). The dolomitic rocks in the vicinity of the Baker Creek Claims closely resemble those found associated with the Kicking-Horse-Monarch Mines. Pseudomorphs of limonite after pyrite have been observed in the white crystalline dolomite in an adit of the showing. The only sulfide mineral found was galena, which occurs in small amounts at the entrance to one of the exploration adits.

Pine Point Mine

The Pine Point area is underlain by the Presqu'ile, Pine Point, Chinchaga, and Mirage Point Formations, all of Middle Devonian Age (Belyea, 1962). The Presqu'ile Formation is a light-colored, coarse, recrystallized, vuggy to massive dolomite, which is generally presumed to have replaced reefal limestone. The other formations consist of anhydrite, sandstone, and variable red bed units. The huge Pine Point ore deposit lies within the Presqu'ile Formation, which is the uppermost dolomite unit in the section. The top of the Presqu'ile dolomites is approximately 1100 feet above the Precambrian basement (Belyea, 1962).

The ore deposits are massive and disseminated bodies of sphalerite and galena. Minerals fill cavities in the crystalline dolomite, which are thought to have been formed by slightly acidic solutions that came into the area prior to ore deposition.

The sphalerite is strongly banded showing colors ranging from light to dark brown. This mineral in places forms colliform structures with stalactitic shapes. In polished section the galena appears to have been deposited later than the sphalerite.

Discussion of Certain Geologic Features

All of the deposits involved in the study are similar in several aspects. The most obvious similarity is their mineralogy. The dominant minerals are sphalerite and galena with very minor amounts of pyrite. One deposit, the Eldon, differs from the rest in respect to the occurrence of chalcopyrite and quartz. The deposits are all located in carbonate rocks, both limestones and dolomite. The limestone at the Hawk Creek deposit is more argillaceous than at the other deposits.

The mineral capable of yielding the most information in a study of this type of deposit is sphalerite. Sphalerite occurs as massive aggregates, which are in some instances banded; as veinlets replacing brecciated dolomite; and as lenses and patches in dolomite or quartz gangue. The massive sphalerite of the Hawk Creek deposits may represent selective replacement of argillaceous bands (Henderson 1954). The sphalerites differ in color from pale yellow, reddish brown, to dark brown with the majority exhibiting a brown to dark brown color. In some thin sections and polished sections growth zoning is revealed by color bands. Many samples of sphalerite from the Pine Point mine show concentric and rhythmic color banding in the crustiform zinc ore.

The order of deposition of the sulfide minerals is often very difficult to determine where the sulfides are randomly intermixed with one another or where they show a rhythmic repetition from band to band. This difficulty was recognized in hand specimens and polished and thin sections.

Relationships between sphalerite and galena suggest that the sphalerite was deposited before the galena in most cases although co-precipitation of the two minerals may have taken place during ore deposition (See Plates II and III). Tiny, well

crystallized cubes of pyrite have been observed in and around the sphalerite in some of the deposits. The usual paragenetic sequence of the minerals as reported by Sims, et al. (1961) and others, is pyrite, sphalerite, and galena respectively. This sequence is accepted on the basis of observations in this study, and on certain findings in the sulfur isotope data of the deposits.

PHYSICAL AND CHEMICAL ASPECTS OF SPHALERITE

Crystallography

Sphalerite (Zn, Fe)S belongs to the Isometric system and the hextetrahedral class. Simple or multiple contact twins or lamellar intergrowths are common on the (111) plane. The high-temperature polymorph of ZnS , is wurtzite which is hexagonal. The transition of pure ZnS to wurtzite occurs around 1020°C but the addition of FeS , CdS and MnS produce a marked decrease in this temperature.

Structure

The structure of sphalerite was determined by Bragg in 1913. The unit cell is face-centered with Zn atoms located at each corner and in the center of each face. Each Zn atom is co-ordinated by four sulfur atoms and each S atom is co-ordinated by four Zn atoms. The S-Zn tetrahedra are all oriented in the same way with a triangular face of the tetrahedron parallel to (111) and the Zn-S tetrahedra oriented in the opposite way with triangular faces parallel to (111). This non-holosymmetric character confers tetrahedral rather than cubic symmetry on the structure. The cell content of sphalerite is four and the space group is $F\bar{4}3m$. The relationship between cubic packing in sphalerite and hexagonal packing in wurtzite may be seen by noting the structure along (111) and (0001) respectively. Layers of Zn atoms have a sequence AB, AB, on wurtzite and ABC, ABC, in sphalerite. In wurtzite, as in sphalerite, the zinc and sulfur atoms are in tetrahedral co-ordination about one another, and the inter atomic distances are similar for each polymorph.

A third polymorph of ZnS is one with a threefold rhombohedral structure. Buck and Strock (1955) suggest that this form is intermediate between sphalerite and wurtzite and is produced by heating sphalerite.

The bonding of sphalerite is largely covalent with some ionic characteristics and the mineral exhibits virtually no metallic characteristics. Sphalerite is isostructural with CdS (Hawleyite), MnS and many other cadmium, zinc, and mercury, selenides

and tellurides. Wurtzite is isostructural with CdS (Greenockite) and other Mn and Cd compounds. Natural sphalerites have been observed to contain co-existing layers of cubic and hexagonal closest packing (Smith, 1955).

Chemistry of the Sphalerites

The sphalerite lattice is highly susceptible to the diadochic substitution of iron, cadmium, and manganese for zinc; up to 39 mole percent FeS, two percent CdS, and nine percent MnS may occur in solid solution in the sphalerite; they usually combine with sulfur in six fold co-ordination in the hexagonal niccolite structure or the halite structure. These substitutions can be explained on the basis of the similarity of the various radii shown in Table 2.

TABLE 2
RADII OF ELEMENTS COMMON TO SPHALERITE

	<u>Zn</u>	<u>Fe</u>	<u>Cd</u>	<u>Mn</u>
Covalent	1.31 Å	1.24 Å	1.48 Å	1.26 Å
Ionic	.71 Å	.74 Å	.97 Å	.80 Å
Normalized	1.19 Å	1.70 Å	1.35 Å	1.13 Å

All of these radii fall within the 15 percent range of variation in which diadochic substitution can occur.

The results of twenty sphalerite analysis are given in Table 3. The sphalerites were analyzed for iron, cadmium, selenium, and manganese by means of X-ray fluorescence equipment at the Geology Department, University of Alberta. The mole percent sulfide has been calculated on the basis that $\text{ZnS} + \text{FeS} + \text{CdS} + \text{MnS} = 100$ percent (as shown in Table 3). Boyle (1963) noted little difference in mole percent sulfide when he calculated it on the basis of his analysis and on the assumption that the analytical sum of the four major constituents was equal to 100 percent. In this study the writer has assumed that there would be little difference in mole percent had they been calculated on the basis of a total analysis for Zn, Fe,

TABLE 3
CHEMICAL ANALYSES OF SPHALERITE

<u>Mine</u>		<u>Sample Data</u>						
<u>Name</u>	<u>Lab. No.</u>	<u>Ref. No.</u>	<u>% Fe</u>	<u>Mole % FeS</u>	<u>% Cd</u>	<u>Mole % CdS</u>	<u>% Mn</u>	<u>Mole % MnS</u>
Kicking Horse	900-1	1	1.10	1.97	.2	.18	.020	.036
	106-1	2	1.23	2.20	.25	.22	.058	.105
	106-1A	3	1.18	2.11	.18	.16	.037	.067
	201-1	4	1.14	2.04	.11	.09	.022	.040
	800-1	5	1.47	2.63	.18	.16	.050	.091
	108-1A	6	1.46	2.61	.22	.20	.081	.147
Eldon	105-2	7	3.40	6.08	.3	.27	.055	.027
	105-2	8	2.63	4.71	.21	.19	.013	.024
	103-1	9	2.05	3.67	.28	.28	.016	.029
	104-4A	10	2.23	3.99	.3	.27	.012	.022
	103-3	11	3.66	6.55	.3	.27	.014	.025
Hawk Creek	1	12	3.21	5.75	.15	.13	.071	.129
	200-1	13	1.53	2.74	.16	.14	.053	.096
	500-1A	14	2.78	4.98	.16	.14	.027	.089
Pine Point	5017-1	15	3.67	6.57	.1	.09	.013	.024
	5017-2	16	2.23	3.99	.15	.13	.012	.022
	5017-3	17	0.90	1.61	.13	.11	.009	.016
	2	18	4.97	8.90	.06	.05	.015	.027
Monarch	2	19	3.1	5.55	.1	.09	.028	.051
	4	20	2.59	4.64	.06	.05	.100	.182

Cd, Mn, and S. The mole percent sulfide was calculated in each case by dividing the weight percent of the element by the atomic weight of that element.

All of the analyzed sphalerites contain iron, cadmium, and manganese in varying proportions. The iron varies from .9 to 4.97 weight percent, the cadmium from .06 to .3 percent and the manganese from .009 to .1 percent. It is seen from the analyses in Table 3 that with the exception of Pine Point sphalerites the amount of iron does not show much variation within one ore deposit.

Strong color zoning and corresponding change in percent iron is apparent in the ores from Pine Point. The average amount of iron in each deposit should indicate the amount of iron available in the solutions depositing the sphalerite and also indicate something about the temperature, pressure, and activity of sulfur.

Cadmium is chemically similar to zinc but is geochemically less abundant. Since sphalerite is the only mineral that will readily accept cadmium the amount of cadmium present in sphalerite might be expected to remain fairly constant within a deposit. This is seen to be the case in the sphalerites investigated.

Manganese on the other hand is geochemically more abundant than zinc and may occur in various amounts in the rock or gangue minerals associated with an ore deposit. Siderite, a mineral common in the Eldon deposit, has been known to contain up to 17 percent MnO (Boyle, 1963). Therefore, one might expect to see variations of manganese in sphalerite due to changes in the local environments in such an ore deposit. Sims and Barton (1961) have suggested that there may be a diadochic substitution of MnS_2 in the pyrite lattice. The manganese content of sphalerite in a given deposit generally increases with an increase in iron, this relationship has been observed by Sims and Barton (1961) and Boyle (1963). As in the case of iron the amount of manganese present should depend on the amount of manganese present in solution, the temperature, pressure and activity of sulfur during deposition.

The amount of selenium present in the sphalerites ranged from 108 to 216 ppm. Little is known about the geochemistry of selenium in sphalerite but it is generally thought that a certain amount of selenium will substitute for sulfur in the sphalerite lattice depending on the activities of other elements in solution and on the crystal-chemical properties of the minerals during deposition. Temperature and pressure would also be important in determining the behaviour of selenium during deposition. It is significant to note that galena co-existing with sphalerite contains up to 1255 ppm. selenium. It is known that the mineral clausthalite (PbSe) forms a complete solid solution series with galena (PbS) (Coleman, 1959). Coleman reports galenas containing as much as 18 mole percent SeS . Thus, galena is capable of incorporating a large amount of selenium, and the sphalerite upper limit of Se substitution appears to be 200 ppm in these deposits.

Coleman et al. (1957) reported a range of 7.09 - 18.00 percent selenium in clausthalite-galena from the Rifle Mine in Colorado. The sulfides occur in sandstone and mudstones of Jurassic age and the selenium is thought to have come from Se-rich tuff and other volcanic rocks interbedded with the sediments. This mine is only one of many in the Utah, New Mexico, Colorado, and Arizona (Four Corners area) that have produced Se-rich sulfide minerals including pyrite, chalcopyrite, marcasite, chalcopyrite and galena.

Table 4 shows the ppm Se for co-existing sphalerites and galena analyzed in this study. The ppm Se of the sphalerites is plotted against the ppm Se of the co-existing galena in Figure 2. Figure 2 shows the partitioning of selenium between the two minerals. It is noted in Table 4 that the range in ppm Se in the Rocky Mountain galenas and sphalerites is rather narrow except for the Eldon deposit. The Eldon galenas range from 1200 - 1255 ppm Se whereas the other Rocky Mountain galenas range from 955-1070 ppm Se. The sphalerites and galenas usually have a small ppm Se range within one deposit.

The selenium abundance data from these deposits suggest that the deposits

occur within a selenium rich ore province. The similarity of the abundance of Se in all those deposits suggest that the deposits might have been formed under similar conditions. The origin of the selenium is unknown although it is possible for solutions to pick up selenium from the rocks through which they travel. The absence of volcanic tuffs and flows in the stratigraphic sections rules out the possibility of deriving selenium from such rocks as was the case in the Four Corners area of the Western United States.

Unit Cell Measurements of Sphalerite

It is a well known fact that iron, cadmium and manganese exert a profound effect on the unit cell dimensions of sphalerites. (Skinner, 1961; Skinner et al., 1959; Kullerud, 1959; and Boyle, 1963).

The cell dimensions of fifteen sphalerites were determined by the X-ray powder method. The X-ray powder photographs were taken with a standard Norelco 114.6 mm diameter camera using cobalt radiation and an iron filter. The films were measured on a vernier with a .05 mm graduation and measurements were estimated to the nearest .025 mm. The d-spacings were obtained from a standard set of 2θ -d spacing conversion tables. The cell edges were determined for each $K\alpha_1$ reflection by using the relationship: $a_0 = d \sqrt{h^2 + k^2 + l^2}$. These calculated cell edges were plotted against a trigometric function

$$1/2 \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$

and the results extrapolated to $\theta = 90^\circ$ (Nelson and Riley, 1945). An example of a Nelson-Riley plot is given in Figure 3. If reflections are measured accurately one should be able to estimate the cell edge to a precision of $0.001\overset{\circ}{\text{\AA}}$ from a straight line plot. The writer has estimated the limit of error involved in measuring the lines on the photos, calculating a_0 and the extrapolation function, and estimating the Nelson-Riley plot, to be $\pm .0010\overset{\circ}{\text{\AA}}$.

TABLE 4

SELENIUM-SULFUR RATIOS FOR SPHALERITE AND GALENA

<u>Deposit</u>	<u>Sample Data</u>		<u>Sphalerite</u>		<u>Galena</u>	
	<u>Lab. No.</u>	<u>Ref. No.</u>	<u>Se ppm</u>	<u>Se/S $\times 10^{-4}$</u>	<u>Se ppm</u>	<u>Se/S $\times 10^{-4}$</u>
Kicking Horse	900-1	1	187	5.66	-	-
	106-1	2	146	4.48	-	-
	106-1A	3	167	4.47	-	-
	201-1	4	216	6.95	-	-
	800-1	5, 5A	155	5.00	955	71.3
	108-1	6, 6A	160	5.75	975	72.8
	100-3	-	-	-	1025	76.5
Eldon	105-2	7	150	4.62	-	-
	103-2	8, 8A	128	3.68	1215	90.7
	103-1	9	109	3.40	-	-
	104-4	10, 10A	120	3.43	1255	93.7
	103-3	11, 11A	138	5.15	1200	82.1
Hawk Creek	1	12	170	5.34	-	-
	200-1	13	166	5.48	-	-
	500-1	14, 14A	210	6.62	960	71.6
Pine Point	5017-1	15	209	6.24	-	-
	5017-2	16	185	5.53	-	-
	5017-3	17	116	3.36	-	-
	2, 100	18, 18A	176	4.98	1080	74.6
Monarch	2, 1	19, 19A	165	4.72	1000	74.6
	4, 3	20, 20A	108	3.73	1030	76.8
Baker Creek	1	-	-	-	1070	79.9
Beaver River	1	-	-	-	1260	94.0

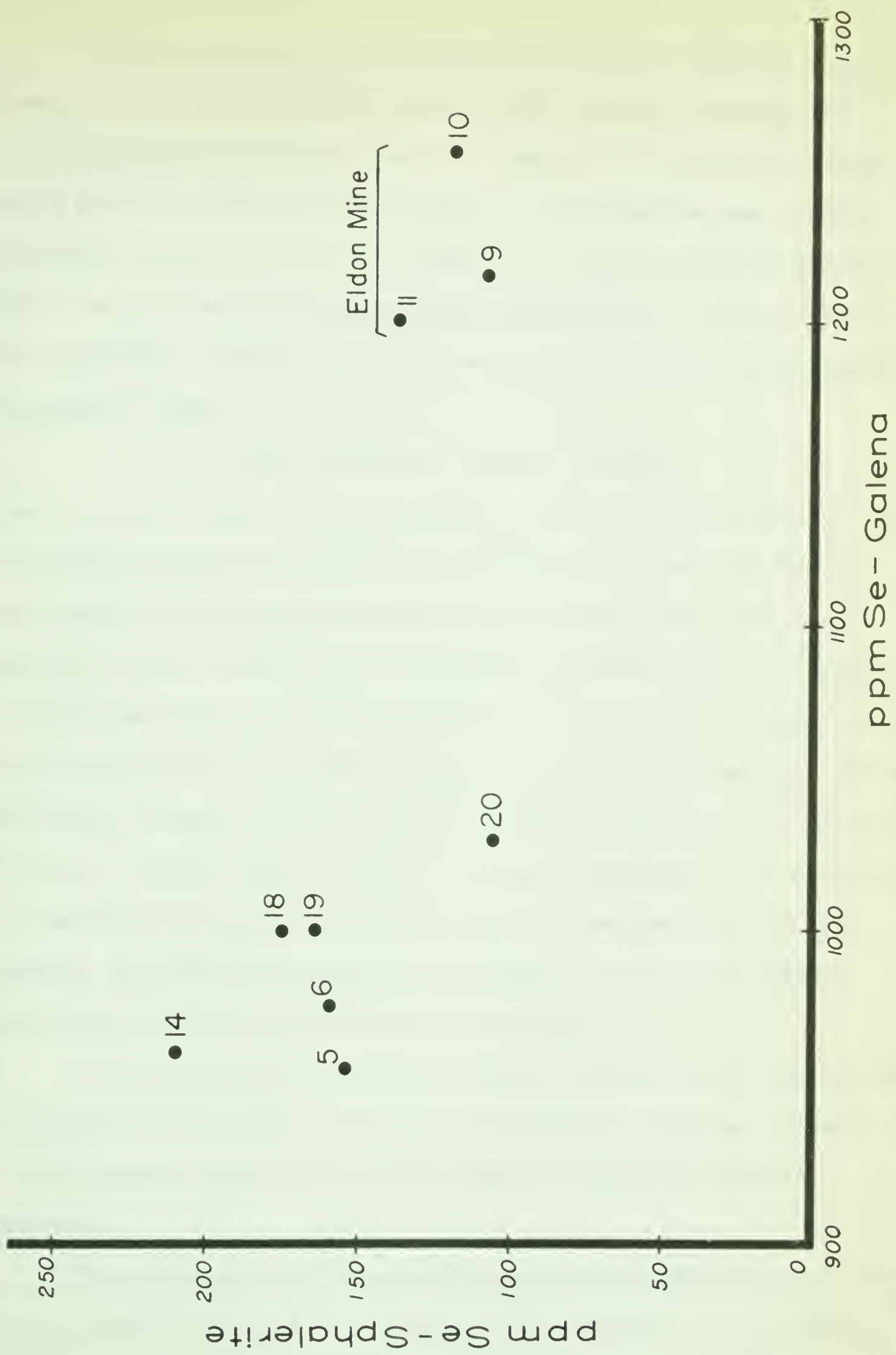


Figure 2. Partitioning of Se between sphalerite and galena

Recent experimental works by Skinner (1961) has shown that the cell edge of sphalerite varies linearly with the content of iron, cadmium and manganese. Skinner measured the cell edges of iron plus manganese-bearing sphalerites and also those of iron plus cadmium-bearing sphalerites. In each case there was a definite linear relation between cell edge and composition. It was concluded that the cell edge of iron plus cadmium plus manganese sphalerites should be linear functions of their compositions. The following relation was used in calculating the cell edges of the sphalerites studied:

$$a_o = 5.4093 + .000456 x + .00424y + .00202 z,$$

where x , y , and z represent the mole percent FeS, CdS, and MnS respectively. The results obtained from the measurements and calculations are presented in Table 5. There is generally good agreement between the two methods with the differences usually well within the limits of error encountered in measuring. Three of the samples show differences greater than the estimated limit of error and there also seems to be a systematic trend for the calculated cell edges to be lower than the measured. Skinner (1961) found the opposite to be the case in his work on natural sphalerites. The reason for the low calculated values is not known although it is possible that there is an error in the analysis of the sphalerite standard, to which all the other sphalerites were compared. The element having the most marked affect on cell edge is cadmium, this element gave difficulty in the wet chemical analysis.

As a result the X-ray fluorescence value of 0.28 mole percent cadmium sulfide was accepted for the standard. An increase in the content of cadmium sulfide by .05 or .1 mole percent would raise the cell dimensions by 0.0002\AA and 0.0004\AA respectively.

The relationship of cell edge and FeS content of the sphalerites involved in this study is shown in Figure 4 along with some data from Skinner, et al. (1959) and Boyle (1963). Both of these authors have shown that FeS content plots linearly against cell edge; this fact is substantiated by the results obtained from this study. One group

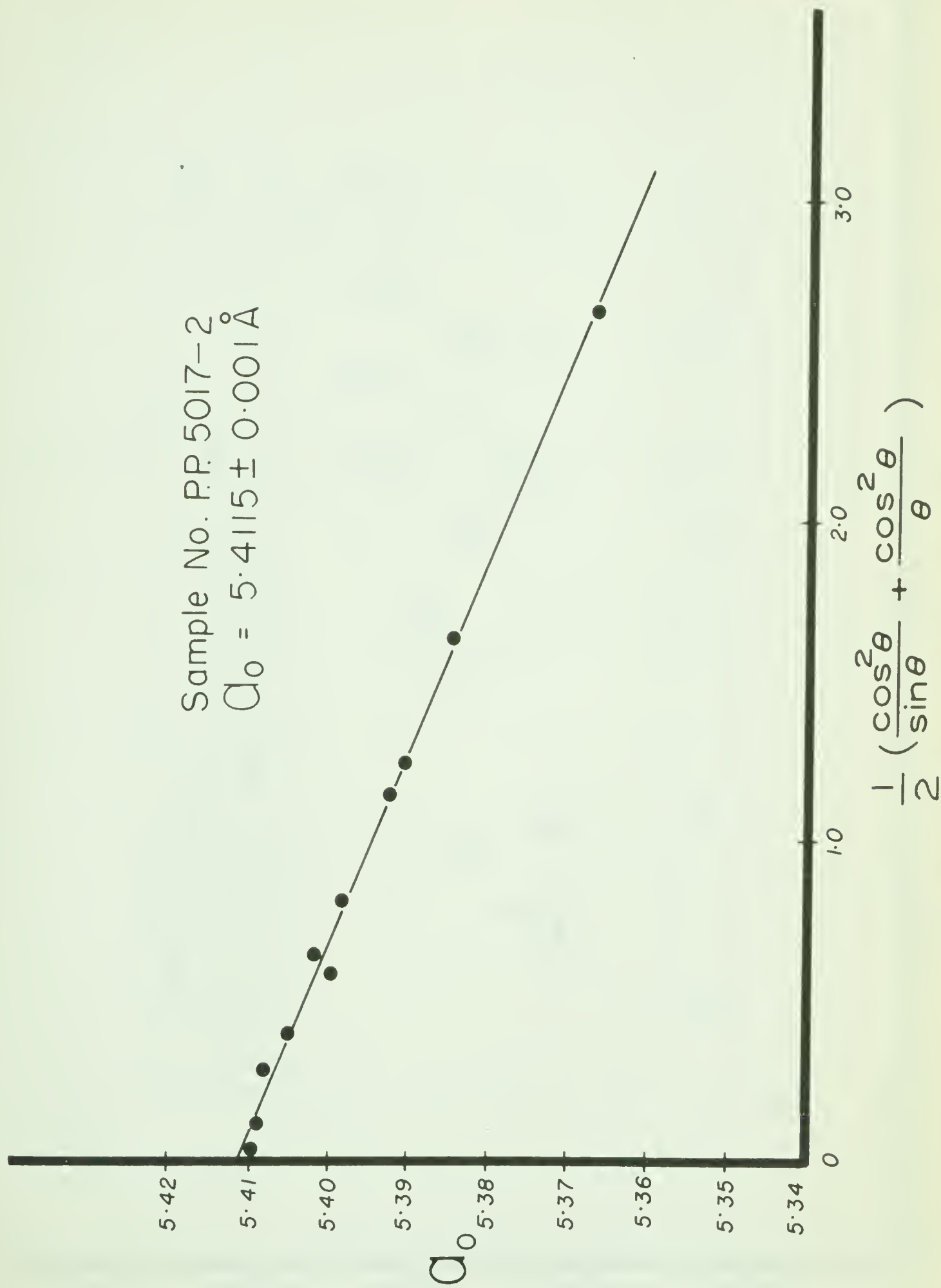


Figure 3. Nelson-Riley extrapolation to find a_0 .

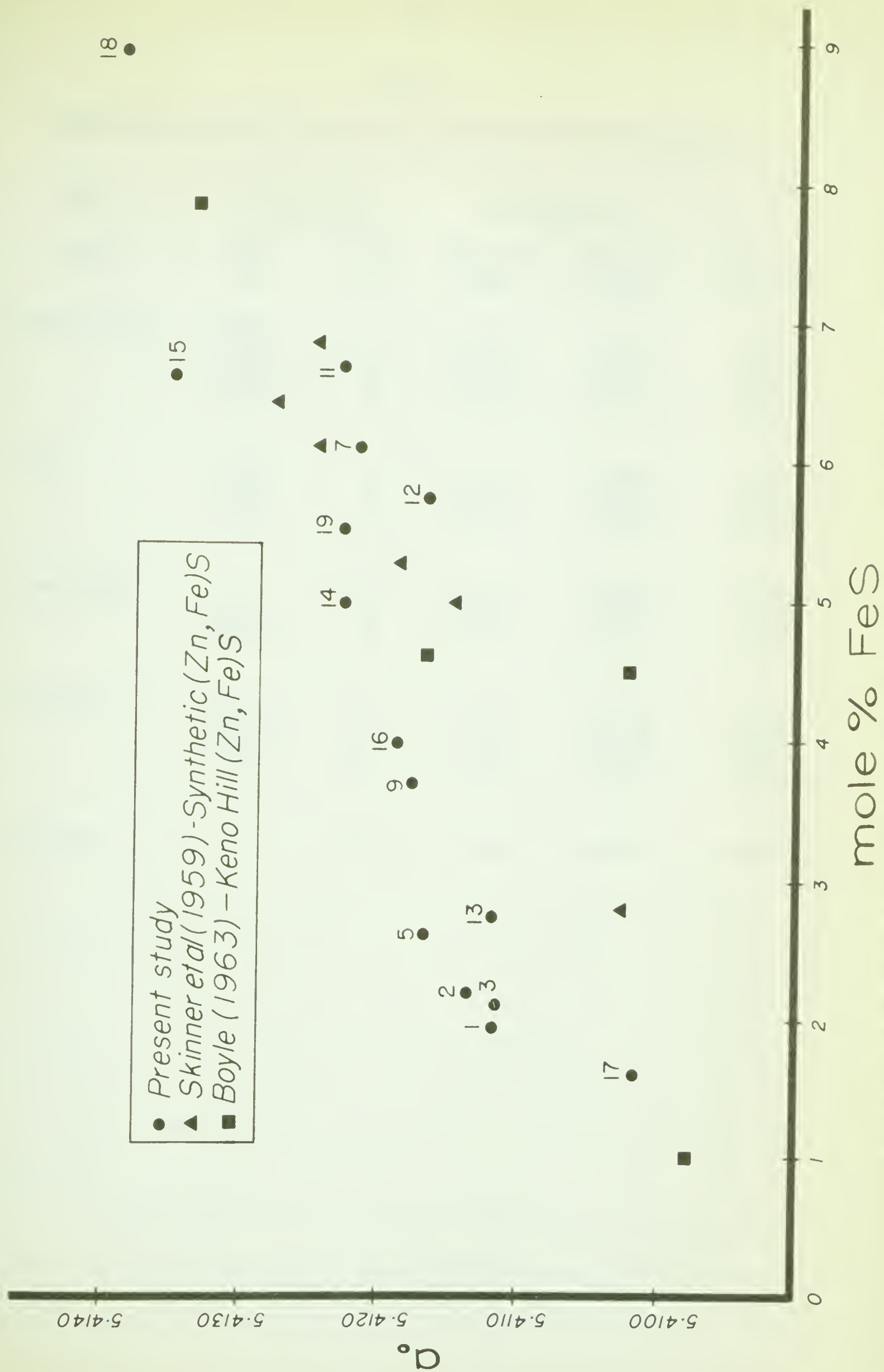


Figure 4. Relationship of measured cell edge and mole percent FeS, corrected for CdS and MnS

TABLE 5

MEASURED AND CALCULATED CELL EDGES OF THE SPHALERITES

<u>Mine</u>	<u>Sample Data</u>		<u>Cell Edge Data</u>		<u>Difference</u>
<u>Name</u>	<u>Lab. No.</u>	<u>Ref. No.</u>	<u>Measured edge</u>	<u>Calculated edge</u>	
Kicking Horse	900-1	1	5.4120	5.4110	-.0010
	106-1	2	5.4125	5.4114	-.0011
	106-1A	3	5.4120	5.4111	-.0009
	800-1	5	5.4125	5.4114	-.0011
Eldon	105-2	7	5.4134	5.4133	-.0001
	103-1	9	5.4130	5.4135	+.0005
	103-3	11	5.4130	5.4135	+.0005
Hawk Creek	1	12	5.4125	5.4128	+.0003
	200-1	13	5.4120	5.4114	-.0006
	500-1A	14	5.4130	5.4123	-.0007
Pine Point	5017-1	15	5.4140	5.4127	-.0013
	5017-2	16	5.4115	5.4118	+.0003
	5017-3	17	5.4107	5.4108	+.0001
	2	18	5.4142	5.4136	-.0006
Monarch	2	19	5.4128	5.4123	-.0005

of sphalerites from the Kicking Horse mine plots abnormally high on the graph in Figure 4; the reason for this behaviour is not known at this time. Since the iron-cell edge relationship conforms with that found by other workers mentioned above, it is concluded that the cell edge does vary linearly with iron. The same relation would of course hold true in the case of cadmium and manganese.

The Problems of Equilibrium in Ore Deposits

Before the properties of mineral phases can be fully utilized in studying the temperature, pressure and chemical environment under which these minerals were formed, an evaluation of the degree of equilibrium present in the ore deposits, at the time of deposition and since deposition, must be undertaken. Equilibrium is defined as the state from which a system has no spontaneous tendency to change (Barton et al. 1963).

In general the three types of equilibrium reactions to be considered in the study of ore deposits are solid state reactions, solution-crystal equilibrium reactions, and reactions in homogeneous aqueous solutions (Barton et al. 1963). Reactions in an aqueous media are thought to produce rapid attainment of equilibrium where those in the solid state would be rather slow. Barton and his co-workers have stated occasions where solid state reactions, particularly those involving galena, chalcopyrite, bornite and digenite, take place rather rapidly. The most important type would be solution - crystal equilibrium reactions. The importance of this is realized in the study of zoned minerals such as sphalerite; it is obvious here that equilibrium did not exist throughout the formation of such a crystal but solution - crystal surface equilibrium must have been attained while each zone was being deposited.

Hydrothermal leaching of a mineral surface by the surrounding solutions becomes important in equilibrium - disequilibrium studies. This phenomenon is present in many ore bodies and may have existed during the deposition of some of

the ores involved in this study. The evidence for this leaching may be seen in the corroded appearance of a mineral phase, and replacement of one mineral by another. The mineral may be redissolving either before or during deposition of the second phase.

In the study of the geothermometry of the western Canadian lead-zinc deposits it is necessary to consider the state of equilibrium between sphalerite and pyrite. Equilibrium between these two minerals is one requirement that must be met before using the temperature-composition diagram for the FeS-Zn System. Pyrite is not a common mineral in these deposits and probably does not account for more than five percent of the sulfide present in any one deposit. In this case it will be assumed that pyrite and sphalerite co-existed under surface equilibrium conditions only. This means that pyrite could have been in equilibrium with a particular zone of sphalerite and out of equilibrium with any other zone in a zoned crystal. Pyrite occurs as well formed crystals, rounded blebs, and bands semi-conformable with sphalerite bands. These textural relations by themselves indicate complex physiochemical relationships between the two minerals during deposition. For this reason, as was previously stated, surface equilibrium is assumed to be the case in the ores.

Geothermometry

Thin section of sphalerite, quartz and calcite were examined for fluid inclusions which might be useful in determining the temperature of formation of the ores. As no inclusions were observed in any of the slides the only other method of temperature estimation is the percent iron contained in the sphalerites. No pyrrhotite was observed in the western Canadian Pb-Zn deposits involved in this study. The only useful assemblage for temperature studies is the sphalerite-pyrite assemblage, and only the minimum temperature of formation can be determined.

Sims, et al. (1961) did a study of the sphalerites from the Central City District, Colorado, and applied this type of approach to temperature estimation. He concluded that the iron content of sphalerite in equilibrium with pyrite was dependent

on (1) other elements present in the depositing solutions; (2) total pressure; (3) temperature and (4) the activity of sulfur. The activity of sulfur was defined as the partial pressure in atmospheres of the gas S_2 .

In this study, as in the Central City study, it is assumed that minor elements such as cadmium and manganese, would have little effect on the iron content and that total pressure by itself plays only a small part in the iron content (Kullerud, 1959). Elements such as selenium and tellurium can substitute for sulfur and could have some effect on the FeS-ZnS relations. These sphalerites contain up to 210 ppm Se, this is equivalent to a S/Se ratio of 1510. At this time it is not known just what effect selenium has on the iron content of sphalerite. The activity of sulfur, henceforth called sulfur pressure, can exert a strong influence in determining how much FeS will enter the sphalerite structure. Sims, et al. (1961) have emphasized the importance of the following reaction:



Kullerud (1959) has calculated that the maximum amount of iron that can enter the sphalerite lattice at 140°C is 4.5 mole percent and 38.9 mole percent at 894°C. Kullerud indicates that the temperature of formation of a sphalerite co-existing with pyrrhotite can be determined within $\pm 20^\circ\text{C}$. He concludes that several reactions could occur between ZnS and Fe_{1-x}S to form (Fe, Zn)S mixed crystals plus Fe_{1-x}S and FeS_2 at any given temperature. It is also noted that at any given temperature and depending on the pyrrhotite-pyrite ratio, all the pyrrhotite could be used up in (Fe, Zn)S mixed crystals and pyrite. If this is the case then the products are (Fe, Zn)S mixed crystals and pyrite, where the composition of the mixed crystals is identical to that obtained when an excess of Fe_{1-x}S is present. Also if the pyrrhotite supply in a system is used up before the sphalerite can take up as much iron as it could have at that temperature the resulting sphalerite would be iron deficient.

In a system containing an assemblage of sphalerite and pyrite in equilibrium with one another, it is seen from Figure 5 that several things can occur if the temperature

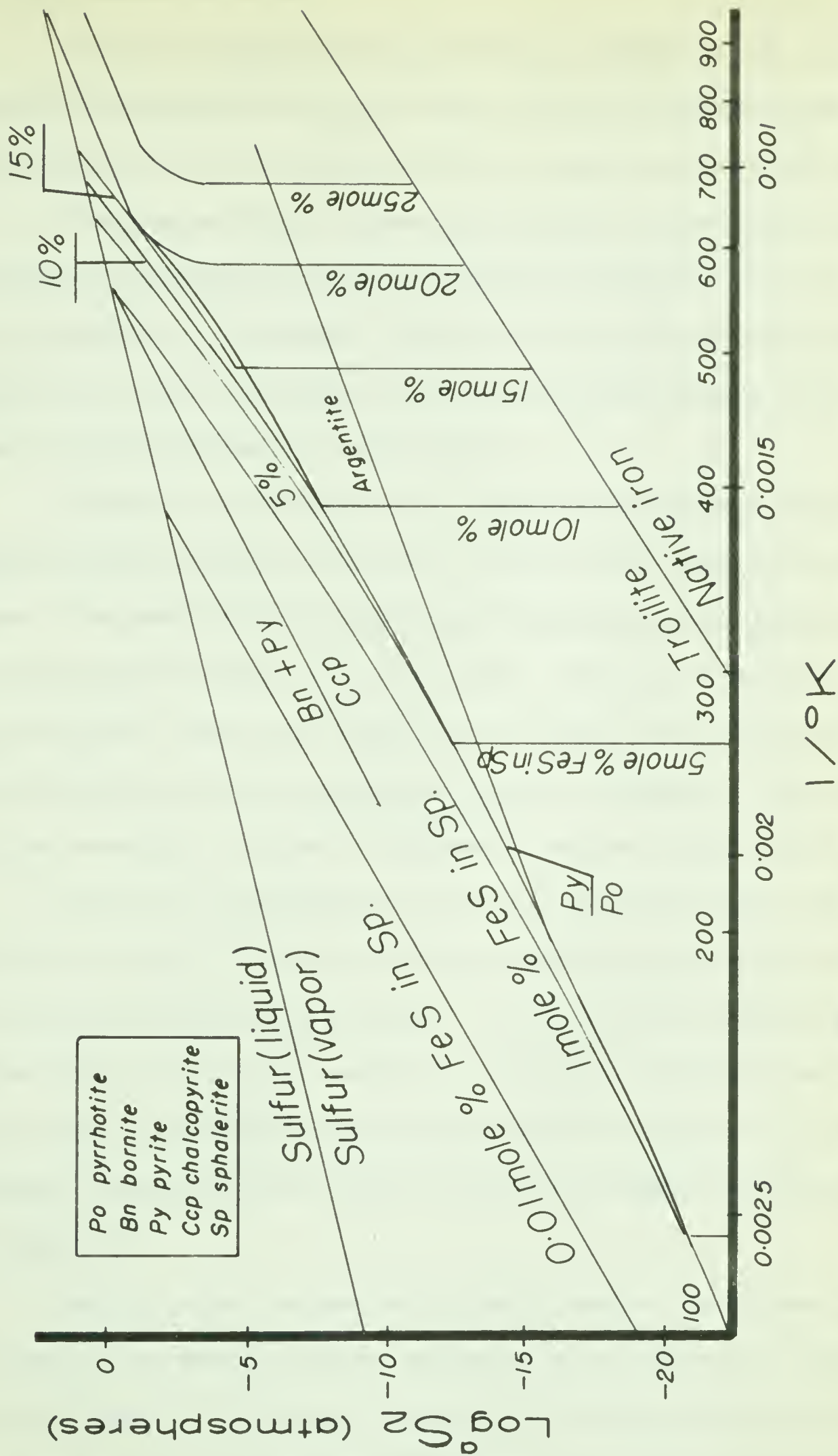


Figure 5. Plot of $\log a_{S_2}$ vs. $1/T^{\circ}K$ for reactions of significance to the low temperature mineralization in Western Canada. (Modified from Sims and Barton 1961).

and sulfur pressure are varied.

1. At a given temperature and sulfur pressure a sphalerite will contain a certain amount of iron and with an increase in sulfur pressure the sphalerite produced will become more and more iron deficient with a continued increase in sulfur pressure.
2. If a system existing at a given sulfur pressure is subjected to a rise in temperature, the sphalerite formed would become increasingly rich in iron if enough iron was available in the solution. If there was not enough available iron, the temperature at which iron ceased to enter sphalerite would become the minimum temperature of crystallization of that sphalerite.
3. If there is a simultaneous rise in temperature and sulfur pressure several things can occur depending on the rate of increase of both temperature and sulfur pressure. The sphalerite formed could conceivably become depleted in iron, the iron content could increase, or the iron content could remain constant if the temperature and sulfur pressure were rising in such a manner as to cause the sphalerite to follow the mole percent FeS₂ composition diagonals in Figure 5. These reactions would be reversible in the case of a decrease in temperature and or sulfur pressure.

In the case of the sphalerites involved in the present study, where no pyrrhotite is present, it is assumed that any pyrrhotite has gone into the formation of iron-bearing sphalerite and into pyrite. Kullerud (1959) has stated that the iron content of sphalerite in a pyrite-sphalerite assemblage could only be as high as that of sphalerite in a pyrrhotite-sphalerite assemblage if at the start the pyrite-sphalerite assemblage contained the exact amount of pyrrhotite needed to saturate sphalerite at that temperature.

Bearing in mind the importance of sulfur pressure, the minimum temperature of formation of the Western Canadian sphalerites can be estimated by using the diagram in Figure 5. This diagram was constructed by Sims and Barton (1961) and shows temperature as centigrade and 1/K plotted against sulfur pressure expressed as the Log S₂ (Richardson and Jeppes, 1952). It is seen from the diagram that an increase

in sulfur pressure would produce sphalerites with decreasing iron contents. Also, a sphalerite could be formed and contain 5 mole percent FeS at any temperature from about 265°C up to about 600°C by raising the sulfur pressure by just the right amount while increasing the temperature. If the iron content of sphalerite is known and the temperature can be determined by fluid inclusion a more definite limit could be placed on the sulfur pressure at that time of sphalerite deposition.

The mole percent FeS of the sphalerites in this study has been used to determine the minimum temperature of formation of each sphalerite. The results are shown in Table 7. If pyrite is present then the minimum possible temperature is equal to the temperature obtained from the FeS-ZnS binary diagram for the system FeS-ZnS (Kullerud 1959).

The average minimum temperature of formations of the sphalerites from each deposit are given in Table 6.

TABLE 6
AVERAGE OF MINIMUM TEMPERATURES OF FORMATION
OF SPHALERITES

Kicking Horse	170°C
Monarch	270°C
Eldon	260°C
Hawk Creek	250°C
Pine Point	260°C

The Kicking Horse and Monarch results are interesting as the two ore bodies give minimum temperatures of 170°C and 270°C respectively; yet the two face one another and are on strike with one another across the Kicking Horse Valley. Workers who have dealt with the geology of these ore bodies (Brown, 1948; and Ney, 1951) have thought the two might have been one continuous body of ore at one time and have implied a common origin for the two deposits. Temperature data indicate a difference of 100°C in the formation of the sphalerites from the deposits, however,

TABLE 7

ESTIMATED TEMPERATURES OF FORMATION OF SPHALERITE

<u>Mine</u>	<u>Sample Data</u>			<u>Estimated Temperature in °C</u>	
<u>Name</u>	<u>Lab. No.</u>	<u>Ref. No.</u>	<u>Mole % FeS</u>	<u>Minimum with pyrite present</u>	<u>Minimum from FeS-ZnS binary</u>
Kicking Horse	900-1	1	1.97	155	155
	106-1	2	2.20	165	165
	106-1A	3	2.11	160	160
	201-1	4	2.04	160	160
	800-1	5	2.63	190	190
	108-1A	6	2.61	190	190
Eldon	105-2	7	6.08	290	290
	103-2	8	4.71	260	260
	103-1	9	3.67	225	225
	104-4A	10	3.99	235	235
	103-3	11	6.55	300	300
Hawk Creek	1	12	5.75	285	285
	200-1	13	2.74	200	200
	500-1A	14	4.08	265	265
Pine Point	5017-1	15	6.57	300	300
	5017-2	16	3.99	235	235
	5017-3	17	1.61	140	140
	2	18	8.90	360	360
Monarch	2	19	5.55	280	280
	4	20	4.64	260	260

it must be remembered that the samples were collected randomly from the mine dumps of the Kicking Horse and from a collection of Monarch Mine minerals at the University of Alberta. The mole percentages of CdS, MnS and the parts-per-million Se in the sphalerites from the two deposits are remarkably similar.

The Eldon and Hawk Creek sphalerite give minimum temperatures which are very similar, the average temperature being 260°C and 250°C respectively. Although the temperatures are similar the deposits are different in several respects. The Eldon contains much vein quartz as its primary gangue whereas the gangue mineral at Hawk Creek is white, crystalline dolomite. The Eldon deposit contains the mineral chalcopyrite along with the usual assemblage, sphalerite, galena and minor pyrite. These differences in mineralogy must be considered before drawing conclusions as to the mode of origin of the two deposits.

The highest minimum temperature obtained from a Pine Point sphalerite is 360°C compared to the lowest obtained temperature of 140°C. The Pine Point sphalerites almost always exhibit distinct color zoning. The color zones vary in width from less than 1 to 30 mm and the transition from zone to zone is usually sharp. Samples 5017-1, 2, 3, are from a typically zoned sphalerite crystal in white dolomite. The inner zone (5017-1) contained 6.57 mole percent iron compared to 3.99 percent in the middle zone and 1.61 percent in the outer zone. Colors of the zones range from dark brown (inner) to light tan (outer). The CdS content of the zones remains fairly constant whereas the MnS content decreases with FeS content. This relationship has been noted by other workers (Sims et al. 1961; Boyle, 1963). It should be emphasized that the fluctuations of FeS in the sphalerites could be a function of the sulfur pressure of the system at the time of deposition rather than a change in temperature or a change of the amounts of iron present in the ore solutions, but the values stated are in any case minimum temperatures.

SULFUR ISOTOPE STUDY OF THE DEPOSITS

Application of Sulfur Isotope Studies

The four stable isotopes of sulfur and their abundance based on the sulfur from the troilite from meteorites are (Rankama 1956):

S^{32}	95.018%
S^{33}	.750%
S^{34}	4.215%
S^{36}	.017%

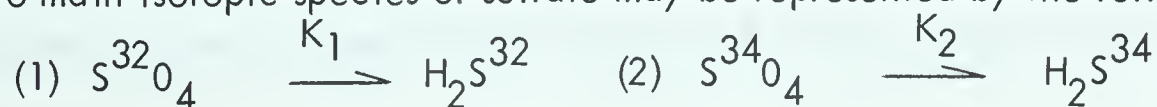
In studies involving sulfur isotopes the ratio of the two most abundant isotopes (S^{34}/S^{32}) is determined. Sulfur isotope data are presented in two forms in the literature. Variations are expressed as the numerical ratio S^{32}/S^{34} or the variation is expressed as the per mil difference from a primary standard in the following fashion:

$$\delta S^{34}\text{‰} = \left(\frac{S^{34}/S^{32} \text{ sample}}{S^{34}/S^{32} \text{ standard}} - 1 \right) \times 1000$$

All samples are compared to the meteoritic value of $S^{32}/S^{34} = 22.21$ or $\delta S^{34}\text{‰} = 0$.

It has been well established that the isotopes of sulfur differ in their chemical properties and are fractionated in certain biological and geological processes (Thode, et al. 1954; Jensen, 1958; Ault, 1959; Sakai, 1957). It has been shown that processes such as inorganic oxidation - reduction reactions and bacterial reduction and oxidation reactions are capable of producing a large fractionation of sulfur isotopes. The kinetic isotope effect in these two processes is extremely important when considering fractionation.

Harrison et al. (1957) studied the kinetic isotope effect in the chemical reduction of sulfate to sulfide (a unidirectional reaction). The reduction to sulfide of the two main isotopic species of sulfate may be represented by the following reactions:



Those authors found that $S^{32}O_4^{+4}$ was reduced 2.2 percent faster than $S^{34}O_4^{+4}$ which is said to be in agreement with theoretical values calculated by statistical mechanics. These authors found the isotopic rate constant ratios (K_1/K_2) to be equal to 1.022.

Nakai et al. (1964) investigated the kinetic isotope effect in the bacterial reduction of sulfate to sulfide and the oxidation of native sulfur to sulfate. They studied this effect with hopes of explaining the large δS^{34} variations of sulfur, in sulfide minerals, that is thought to be of bacteriogenic origin. In their reduction experiments they used sea water and bottom sediments containing the anaerobe Desulfovibrio desulfuricans and by obtaining a simulated anaerobic environment they attempted to duplicate nature during the experiments.

They defined the rate constants $\left(\frac{K_1}{K_2} \right)$ for equations (1) and (2) as:

$$K_1 t = \ln \frac{(S^{32}O_4^o)}{(S^{32}O_4)}$$

$$K_2 t = \ln \frac{(S^{34}O_4^o)}{(S^{34}O_4)}$$

where $(S^{32}O_4^o)$ and $(S^{34}O_4^o)$ are the initial concentrations of $S^{32}O_4$ and $S^{34}O_4$ respectively, and $(S^{32}O_4)$ are the concentrations of $S^{32}O_4$ and $S^{34}O_4$ at time t . They calculated the K_1/K_2 ratios from the relationship:

$$R_{SO_4} = R_{SO_4}^o [F^{1 - (K_2/K_1)}]$$

where R_{SO_4} and $R_{SO_4}^o$ are the S^{32}/S^{34} ratios of sulfate at time t and time 0 respectively, and F is the ratio of the amount of residual sulfate at time t to initial sulfate at time 0. The K_1/K_2 values were rather constant and averaged 1.020 which is nearly the same as the results from Harrison and Thode's inorganic chemical

reduction experiments. They further showed that the fractionation factor

$$r = \frac{R_s}{R_{SO_4^{+4}}}$$

where $R_s = S^{32}/S^{34}$ of the produced sulfide and $R_{SO_4^{+4}} = S^{32}/S^{34}$ of the remaining sulfate, exceeds K_1/K_2 by a considerable amount. They measured values of r ranged from 1.043 to 1.062, although the fractionation factor would approach infinity if the reaction neared 100 percent completion. Therefore, it seems probably that, under the right conditions (in a closed system), very large fractionation factors could occur in nature.

Nakai et al. (1964) also showed that native sulfur and pyrite could be oxidized by bacteria of the genus Thiobacillus. They found that the produced sulfate was enriched in S^{32} with respect to the reactants, sulfur and pyrite, by as much as 1.5 ‰ for native sulfur and .4 ‰ for pyrite. They found the fractionation factor remained constant during oxidation and the total fractionation occurring depended on the time involved in the reactions.

From this discussion the importance of biogenic reactions in fractionating sulfur in sediments is evident. It has been proven that sulfate-reducing organisms produce H_2S gas that is lighter isotopically than the residual sulfate. It should be remembered when considering geologic phenomenon in light of this type of fractionation that the sulfide need not be greatly enriched in S^{32} with respect to the meteoric value as is suggested by the Colorado Plateau sulfides (Figure 6). Since sulfate can be already enriched in the heavier S^{34} the sulfide produced from the reduction of it should be lighter than the sulfate but can still be enriched in S^{34} with respect to the meteoritic value of ‰ $S^{34} = 0$. It is also apparent that a highly variable S^{34} composition is characteristic of biogenically produced sulfur. A system undergoing fluctuating environmental conditions and varying oxidation-reduction reactions could show extreme variations in isotopic composition.

Sulfur isotope abundance data for sulfide minerals from ore deposits having varying genetic origins and data from sulfur found in other sources other than sulfides is given in Figure 6. It is evident from these abundances that considerable variation of sulfur isotopic composition exists in ore deposits. The S^{34} composition of sulfides of undoubted igneous origin is usually very close to the meteoritic value whereas sulfur from sulfides of questionable origin show considerable variation on both sides of the meteoritic value.

If hydrothermal solutions are collecting in the cupola of a magma chamber during the crystallization of this magma then the isotopic composition of any sulfur in the system would probably become homogenized with time, this homogenization would most likely occur in the case of a separate sulfide melt segregating from the magma although some fractionation might occur between the two phases. Subsequent release and deposition of sulfides from the solutions and or sulfide melt would probably result in very little fractionation. Whether fractionating occurs during transportation and deposition of ore forming constituents is not known. Rafter, et al. (1958) have investigated the sulfur isotopic variation in New Zealand geothermal bore water. This discharge was found to contain about thirty percent by weight of steam but calculations established that the liquid consisted of only a water phase in the source underground. The sulfate which followed the water phase was enriched in the heavier isotope S^{34} by as much as 1.7% with respect to the sulfide which went along with the vapor phase. These New Zealand data have indicated the possibility of fractionation occurring between the separation of a gas phase from a liquid phase during ore solution transport.

Berner (1962) has studied black iron sulfide in recent marine sediments and has postulated the formation of these iron sulfides as being precipitated by the reaction of H_2S , produced by sulfate-reducing bacteria, with iron compounds present in the sediments. The result is a poorly crystalline form of tetragonal FeS tentatively called hydrotroilite ($FeS \cdot nH_2O$). With burial and compaction this should be converted to pyrite with the addition of more sulfur.

Jensen (1962) has cited an experiment where anaerobic bacteria of the genus Desulfovibria reduced sulfate present in Long Island Sound, Connecticut, marine mud. The H_2S emitted was depleted in the heavy isotope with respect to the residual sulfate. He found that the H_2S reacted with ferric iron so rapidly that little H_2S was emitted from the muds as the free gas. He demonstrated that copper sulfides were formed as rapidly as the iron sulfides.

Experimental Procedure

Thirty-one sulfide minerals were prepared for mass spectrometric analysis, by a method described by Thode (1954). Each sphalerite, galena, pyrite, and chalcopyrite sample was prepared by treating with concentrated nitric acid and liquid bromine. After standing for eight or more hours the mixture was evaporated to dryness, concentrated hydrochloric was added and the mixture evaporated to dryness again. The soluble sulfate was dissolved in hydrochloric acid and demineralized water, iron was precipitated with ammonia, and the sulfate precipitated as barium sulfate by adding barium chloride solution.

The barium sulfate was then reduced to hydrogen sulfide by boiling in a solution of hydroiodic, hydrochloric and hypophosphorous acids in a refluxing apparatus. The hydrogen sulfide was precipitated as cadmium sulfide in a cadmium acetate solution and then converted to silver sulfide by adding silver nitrate solution.

The silver sulfide was washed with ammonia to remove any chlorides, centrifuged, and oven-dried. It was then burned to sulfur dioxide in a quartz tube in a stream of purified oxygen, condensed in liquid oxygen traps and swept through a dry-ice-acetone cooled trap to remove water. It was then condensed in a liquid air-methanol cooled trap and pumped to remove any carbon dioxide. It was finally condensed in a break-seal sample holder where it was stored until analyzed in the mass spectrometer.

To test the efficiency of the reduction procedure the Volhard back titration

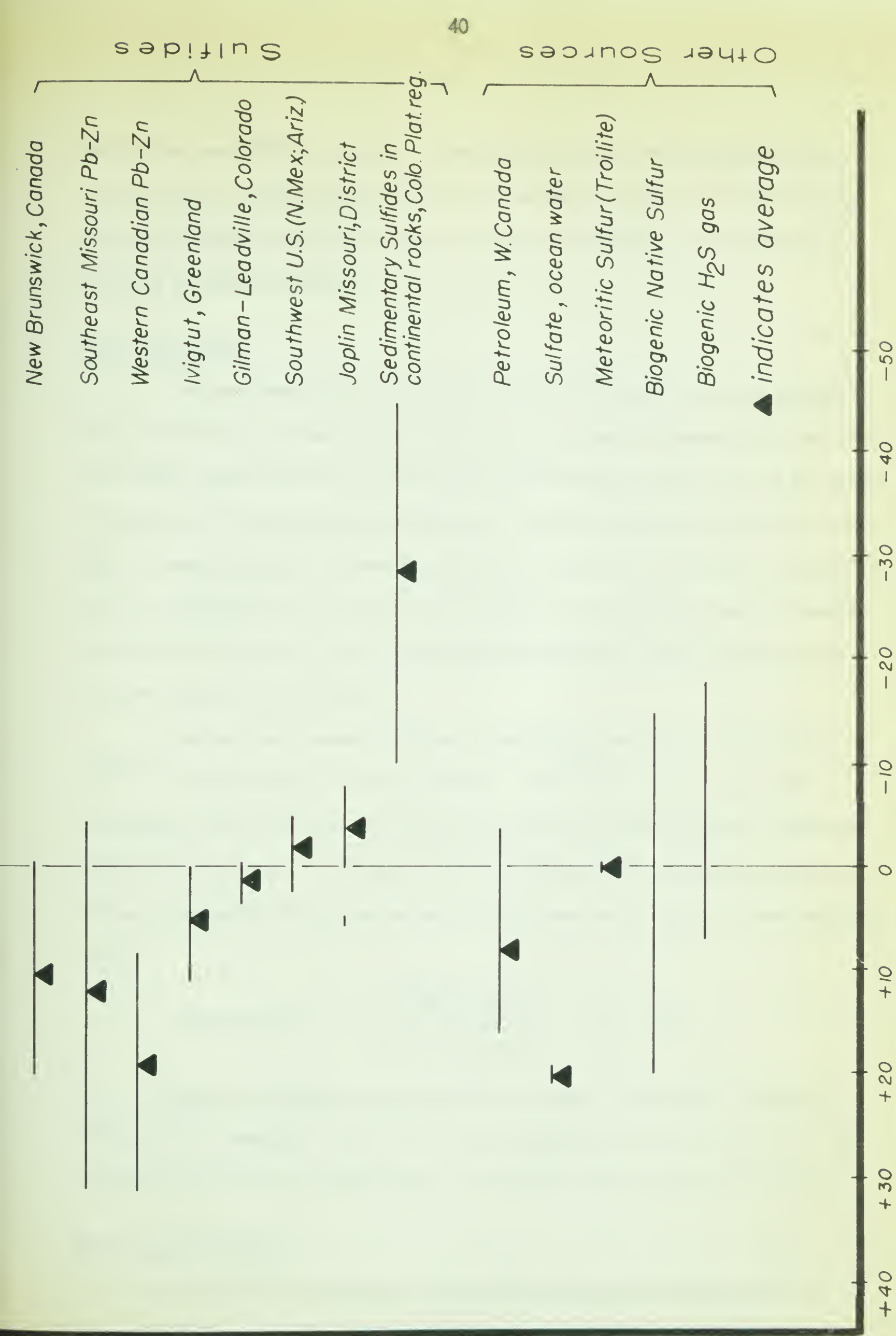


Figure 6. Sulfur isotope abundance data from sulfides and other sources. (Ault 1959; Thode, et al. 1958)

method was used (Kolthoff, 1952). A standardized silver nitrate was added from a burette and the excess was back titrated with ammonium thiocyanate solution using a 40 percent ferric ammonium sulfate solution, as the indicator. The recovery in this case was about 98 percent.

Mass Spectrometry

The mass spectrometer used was a 12 inch 90° magnetic analyzer equipped for the simultaneous collection and analyses of ion currents of masses 64 and 66. The ion currents were amplified by vibrating reed electrometers and the ratio of the output voltages from the vibrating reed electrometers were periodically displayed with a five figure integrating digital voltmeter-radiometer and printed with a digital recorder. By using two magnetically controlled valves, the flow of gas into the mass spectrometer can be switched instantly from a standard reference sample of sulfur dioxide to the unknown sample being analyzed.

The mass spectrometer analyses are reported as per mil deviations of the S^{34}/S^{32} ratio of a sample from the standard. Ten S^{34}/S^{32} ratios were printed alternately for the unknown and standard and six sets of sample-unknown ratios were obtained during each run. The mean ratio was calculated for each set and the ratio of the printed ratios of the unknown and standard were calculated on a time corrected basis.

$$\text{Uncorrected } \delta = \left(\frac{S^{34}/S^{32} \text{ unknown}}{S^{34}/S^{32} \text{ standard}} - 1 \right) \times 1000$$

This value obtained is corrected for the oxygen isotope effect (Mass 64- $S^{32} O^{16} O^{16}$; Mass 66- $S^{32} O^{16} O^{16}$), by multiplying the δ value by 1.095. The standard deviation for each individual run is usually around .01 percent (Table 8).

Results and Discussions

The results of the isotopic analyses of the thirty-one sulfide samples are presented in Figure 7 to show the variations in isotopic composition from deposit to

deposit and also to show variations within each ore deposit. Of particular significance are the variations between two co-existing mineral species in a hand sample. The isotopic analyses of the different mineral species of each deposit are tabulated in Table 8. Co-existing sulfide phases are connected by a line in Figure 7.

It is seen that the δS^{34} values are all positive with respect to the meteoritic reference and range from 8.08 mils to 31.36 mils. The greatest variation in sulfides from one deposit occurs in the Kicking Horse where two sphalerites from different hand specimens gave per mil values of 20.14 and 31.26.

Two Pine Point sphalerites gave a difference of 6.8 mil. The reasons for these rather large difference within one deposit is not known although it is obvious from the complex and intricate textures observed in the Pine Point sphalerites that this deposit must have had an extremely complex depositional history.

The greatest δS^{34} variation of two co-existing sulfide minerals occur in sample #4 from the Kicking Horse mine. Two ages of sphalerite, a dark brown iron rich phase and a yellow less iron rich phase, co-existed, with galena, in a dolomitized limestone breccia. The first sphalerite phase (iron rich) gave a δS^{34} value of 31.26; the yellow phase gave a value of 29.56 and the galena a value of 25.85. The difference between the dark sphalerite and galena is 5.41 mils. It is interesting to note here the lesser degree of enrichment of S^{34} follows the paragenetic sequence of deposition if the sulfur responsible for the sulfides is considered to be in a reservoir which is slowly being depleted in S^{34} due to sulfide crystallization. This interpretation assumes that the less energetic S^{34} would be incorporated into sulfide production first thus enriching the residual solution in S^{32} . A unidirectional change in the isotopic composition of ore forming solutions can be visualized in either an open system with dropping temperature or in a closed system. In seven cases out of eight in the present study, where the sulfur in co-existing sphalerite and galena were analyzed the sphalerite sulfur was enriched in the heavier S^{34} with respect to galena. Three pyrites from the Hawk Creek deposit, along with co-existing sphalerite and/or galena also

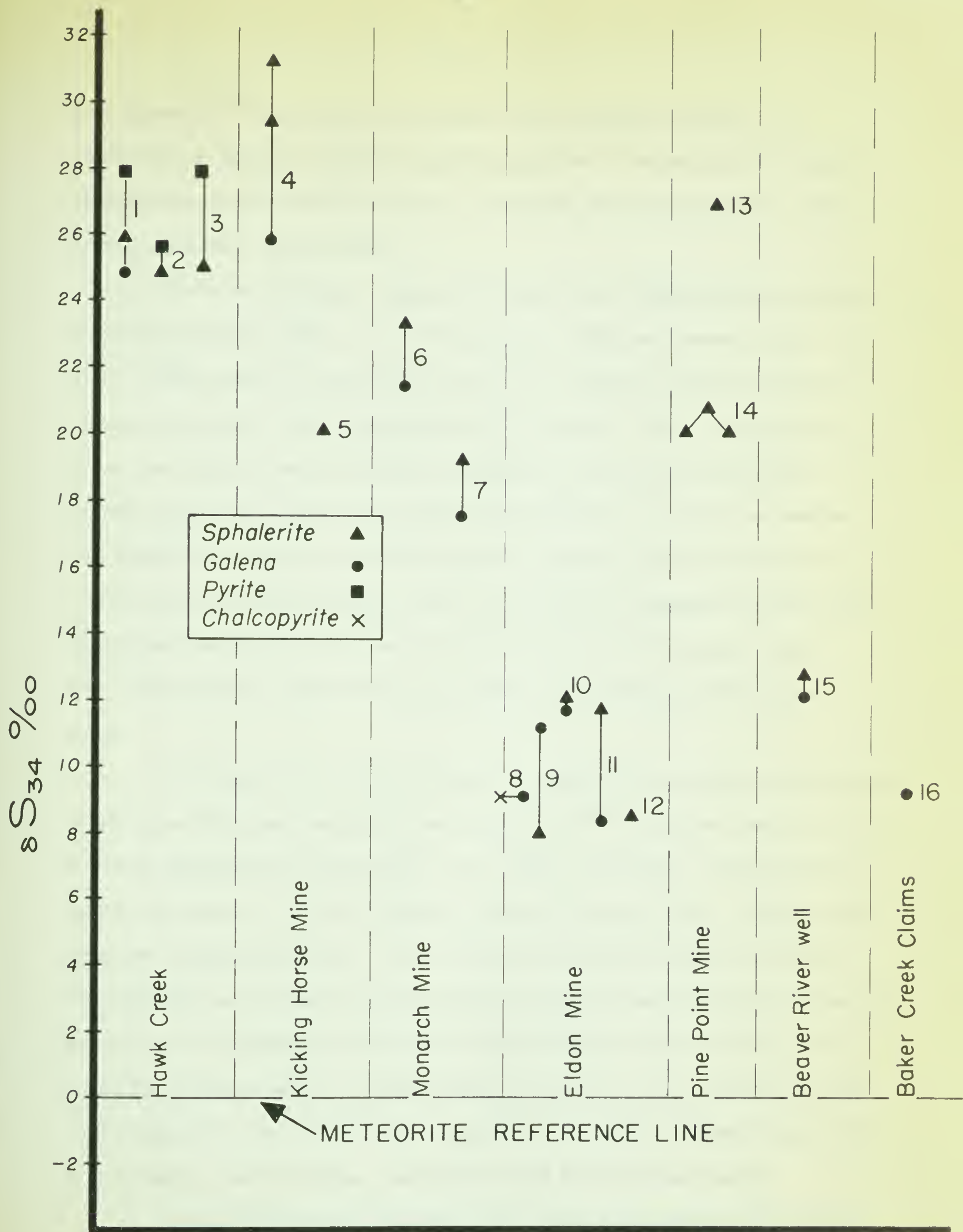


Figure 7. Sulfur isotope data from Western Canadian sulfides.

gave higher δS^{34} values respectively than the other adjacent sulfides. If a unidirectional change in isotopic composition with time is assumed and the sequence of deposition, pyrite-sphalerite-galena, is accepted, then the paragenetic order of sulfide deposition is substantiated.

Variations of isotopic composition in co-existent sulfide minerals has been demonstrated before (Ault, et al. 1960; Kulp et al. 1956; and Jensen, 1958). Ault et al. (1959) gives δS^{34} values of 16.2 and 7.7 for adjacent sphalerite and galena respectively from the Northwestern Illinois Pb-Zn district. The same authors have shown that sulfide minerals of different composition which have crystallized in intimate association need not have appreciable differences in isotopic composition. This suggests that isotopic fractionation doesn't necessarily have to accompany the crystallization of sulfide minerals. Ault et al. (1959) have suggested that this lack of fractionation of sulfur compared to abundant fractionation of oxygen isotopes may be due to similar atomic bonding of sulfides and smaller mass differences in sulfur.

It has been fairly well established that sulfide sulfur of magmatic hydrothermal origin shows rather small isotopic variations and the δS^{34} values are usually within 5 mils of the meteoritic standard (Ault, et al. 1960, and others). Examples of this type are numerous, i.e. Butte, Montana; Gilman, Colorado; Sudbury, Ontario; and Quemont, Quebec; and others. These .5 percent deviations indicate that most of those sulfides were not derived directly from the mantle (a geochemically homogeneous source) but have probably come from local magma chambers where the sulfur source would not be large enough to include average crustal sulfur, but would only be close to the meteoritic value of $\delta S^{34} = 0$. It would be reasonable to assume in some cases that the magma could have been sedimentary rocks that have been melted.

The results obtained in this study show clearly the deviation of the isotopic values from the crustal mean so the writer deems it reasonable to conclude that the sulfur in these Rocky Mountain and Plains deposits is not magmatic. As shown in

TABLE 8
SULFUR ISOTOPE DATA

<u>Location (Mine)</u>	<u>Sample Data</u>			<u>Isotope Data</u>		
	<u>No. in Table</u>	<u>Lab. No.</u>	<u>Mineral</u>	<u>Description Table</u>	$\delta S^{34}\text{‰}$	<u>Standard Deviation (\$)</u>
Hawk Creek	1	500-1	Pyrite	A	27.87	.12
	1	500-1A	Sphalerite	A	25.91	.20
	1	500-2	Galena	A	24.80	.13
	2	300-1	Pyrite	B	25.63	.09
	2	400-1	Sphalerite	B	24.86	.07
	3	2	Pyrite	C	27.90	.23
	3	1	Sphalerite	C	25.07	.12
Kicking Horse	4	800-1	Sphalerite	D	31.26	.25
	4	800-1	Yellow			
			Sphalerite	D	29.56	.24
	4	800-1	Galena	D	25.85	.09
	5	201-1	Sphalerite	D	20.14	.12
Monarch	6	2	Sphalerite	E	23.44	.31
	6	1	Galena	E	21.80	.37
	7	3	Galena	E	17.63	.05
	7	4	Sphalerite	E	19.14	.20
Eldon	8	104-1	Chalcopyrite	F	9.18	.17
	8	104-1	Galena	F	9.16	.15
	9	103-1	Galena	G	11.25	.19
	9	103-1	Sphalerite	G	8.06	.13
	10	103-2	Galena	G	11.83	.15
	10	103-2	Sphalerite	G	12.15	.09
	11	103-3	Galena	G	8.38	.15
	11	103-3	Sphalerite	G	11.69	.10
	12	105-2	Sphalerite	H	8.57	.10
Pine Point	13	5017-1	Sphalerite	I	20.28	.33
	13	5017-2	Sphalerite	I	20.99	.35
	13	5017-3	Sphalerite	I	20.02	.08
	14	2	Sphalerite	J	26.95	.05
Beaver River	15	1	Sphalerite	K	12.84	.10
	15	1	Galena	K	12.20	.40
Baker Creek	16	1	Galena	L	9.20	.13

TABLE 9
DESCRIPTIONS OF ORE SAMPLES

<u>Code</u>	<u>Description</u>
A	Coarse sphalerite, galena, and pyrite in dolomite.
B	Ruby sphalerite with pyrite in coarse dolomite.
C	Brown, fine-grained sphalerite with pyrite in grey argillite; banded ore.
D	Brown, yellow, coarse sphalerite with coarse galena in grey and white, fine to coarsely crystalline dolomite.
E	Reddish brown coarse sphalerite with coarse galena in grey dolomite.
F	Coarse chalcopyrite with minor galena in white quartz.
G	Coarse to fine brown sphalerite with galena in sericite and quartz matrix.
H	Ruby sphalerite with minor galena in quartz.
I	Zoned sphalerite crystals in white, coarsely crystalline dolomite.
J	Banded, variable color (tan-brown) sphalerite with galena.
K	Sphalerite with galena in fine-grained dolomite, veined by white crystalline dolomite.
L	Galena in fine-grained, grey dolomite veined by white crystalline dolomite.

Figure 6 the sulfur in these deposits is analogous to that of the Mississippi Valley type deposits. The Mississippi Valley sulfides show a wide range in isotopic ratios ranging from about 0 to 3.5 percent whereas the Western Canadian Plains and mountain deposits range from about 0.8 to 3.2 percent with an average of δS^{34} value of about 19.1. The deposits involved in this study are similar to the Mississippi Valley type deposits in many respects, a few of which have been listed below:

1. The sulfide ore bodies usually are emplaced in carbonate rocks, particularly dolomite.
2. Both regions are devoid of any igneous rocks which might have been the obvious source of mineralizing solutions.
3. Sulfide deposition is usually controlled by minor roll structures and breccia zones.
4. The mineralization, usually consisting of sphalerite galena, and pyrite, is very simple in most cases.
5. Sulfide ore shoots may be conformable with the bedding of the country rocks; often this is replacement rather than intrastrata deposition.

It should be noted that recent work in the Upper Mississippi Valley area indicates that certain cryptovolcanic structures, diatremes and breccia pipes have been found in the subsurface throughout the district (Erickson, 1965). An igneous body which resembles a volcanic breccia pipe has been found in the subsurface of N.W. Alberta. The bottom hole temperature in this well was 87°C at a depth of 1396 feet. This indicates a geothermal gradient of 329°C per mile. This extremely anomalous gradient is probably a local phenomenon since another well in the vicinity indicated temperatures of 50°C at 5475 feet. This figure is more reasonable but is still above the normal geothermal gradient of 40°C per mile.

In the results from Western Canadian deposits it is seen that the Eldon mine sulfides have δS^{34} values somewhat lower than the other deposits. As was mentioned earlier this deposit has a mineralogical assemblage somewhat different from the others in this study (i.e. the presence of chalcopyrite as an ore mineral and quartz as gangue). Sericite, a micaceous mineral often accompanying hydrothermal mineralization, is also

present in the Eldon deposit. The mineralogy and the lower S^{34} enrichment tend to set this deposit apart from the rest, in that true hydrothermal and possible magmatic affinities are more pronounced. The Baker Creek claims lie on the east side of the Bow Valley opposite the Eldon Mine. Mineralization is very sparse here and only a small amount of galena was found and analyzed isotopically. The δS^{34} value of the single galena falls well within the range of the Eldon galenas. Copper mineralization has also been reported on Copper Mountain, 12 miles N.W. of Banff, Alberta (Dawson 1885). There appears to be a zone of Pb-Zn-Cu deposits roughly parallel to the Bow Valley in the Banff-Lake Louise area, which is rather distinct from the Pb-Zn districts farther east in the Hawk Creek and Field, British Columbia areas. This distinction is recognized in the sulfur isotope ratios and the differences in mineralogy. If the sulfur was derived from a source to the west and is a product of remobilization by a driving heat force the lightest sulfur, isotopically, would be found in the eastern most deposits, which is the case.

The high δS^{34} values of all the sulfides studied pose a problem concerning the source of sulfur for mineralization. A magmatic source for the sulfur has been ruled out on the basis of the analyses, therefore, the only other likely source remaining for sulfur determination is the rock or connate water in the strata. As previously mentioned it is well known that sulfur isotope fractionation can readily occur during reduction of sulfate by certain anaerobic bacteria; this reduction producing residual sulfate enriched in S^{34} and sulfide enriched in S^{32} . This residual sulfate can have δS^{34} values much greater than sea water sulfate which has an average δS^{34} value of 20.2. Extreme δS^{34} variations in marine sulfate and sulfide in the Black Sea has been demonstrated by Vinogradov et al. (1962). They report δS^{34} values for sulfides ranging from - 63.2 to + 1.8 mils and + 1.8 to around + 40 for sulfate. The sulfide in this case was in the form of hydrotroilite and pyrite.

Sulfur could have at one time been present in marine sediments of the Rocky Mountain and Liard Basin region in the form of organic sulfur. Kaplan et al. (1963)

reports up to 3.3 weight percent sulfur in certain marine algae and marine animals in recent marine sediments off the coast of southern California. The sulfur in the algae had an average δS^{34} value of + 19.6 mils and the marine animals sulfur an average value of 15.3 mils. The presence of sulfur bearing plant and animal life in the Cambrian-Ordovician and Devonian rocks, in which the ore deposits lie, is not unlikely. Sulfur in pyrite or other sedimentary sulfides could also serve as a source of sulfur although pyrite from sediments is usually enriched in S^{32} with respect to sea water but not necessarily enriched in S^{32} with respect to the meteorite standard. In other words, hydrogen sulfide derived from very heavy sulfate in sedimentary rocks could have δS^{34} values of one to two percent. The work of Kaplan et al. (1963) shows quite well that marine rocks could be expected to contain sulfur showing wide variation in δS^{34} values. Sulfur in the form of free sulfur, organic sulfur, pyrite sulfur, acid volatile sulfide (hydrotroilite), sea water sulfate, and sulfur from marine plants and animals could exist in the rocks. At the time of deposition it could conceivably retain most of this sulfur until hydrothermal leaching occurred or until it was remobilized by a heat source. In the case of ore formation the only other component needed would be the metallic ions and the right physico-chemical environment to precipitate sulfide minerals.

Thode et al. (1958) have determined the sulfur isotope variations of petroleum sulfur from oils found in certain Western Canadian and American oilfields. He found the δS^{34} values varied up to 4 percent. Of particular interest are the δS^{34} values for petroleum sulfur and hydrogen sulfide of Devonian and Lower Cretaceous oils of Alberta. The Devonian oils gave δS^{34} values of up to 4 percent, the average being about 1.3 percent. Oil samples from the large Leduc oil pool showed remarkable consistence in their sulfur isotopic composition (average $\delta S^{34}_{\text{‰}} = 12$).

The source material for petroleum is organic and the oil probably comes from

the decomposition of marine plants. Anaerobic bacteria may be very active promoters of petroleum formation in the bottom of seas where reducing conditions would be prevalent. Sulfur in petroleum could come from the reduction of inorganic (sea water) sulfate as well as from marine plant and animal life. It is important to note that sulfur from either source could be isotopically heavy sulfur such as that found in Devonian and Lower Cretaceous oil pools in Alberta.

The similarity between the δS^{34} values of Alberta petroleum and the sulfur in the western Canadian Pb-Zn deposits cannot be overlooked. The Pine Point sulfides are especially important in this regard since they occur in Devonian reef carbonates (Elk Point Group of Nahanni carbonate sequence) and show δS^{34} values similar to the Devonian oils ($\delta S^{34} = 20$). This example of isotopic variation in petroleum, especially petroleum of Western Canada, is given to demonstrate that sulfur having rather high δS^{34} values can certainly be found in carbonate rocks similar to those containing the Pb-Zn ore bodies in this study.

ORE GENESIS

The origin of these ore deposits and others similar to them (Mississippi Valley, Upper Silesia, and others) has long posed a problem to students of mineral deposits. It is one that will not be resolved before much time and effort has been expended into the detailed investigation of many aspects of the deposits. Much has been published on the physical and chemical aspects of ore deposition of the type encountered in this study (Lindgren, 1933; Barton, 1957; Bateman, 1950; Park, et al. 1963; Noble, 1963; Brown, 1965; and many others).

At present there are three general theories of ore genesis that should be considered when searching for the origin of this type of ore deposit (Brown, 1965).

1. The lateral secretion theory suggest that the ores are concentrated from the country rocks by circulating waters moving laterally or vertically. These waters are generally thought of as either being hot or cold but it is now generally accepted that the water has been heated up by some source such as burial or the proximity to igneous rocks. Knight (1957) postulates the "source bed theory" as the basis of ore genesis for some ore deposits. He advocates deriving these sulfides from rocks containing syngenetic sulfides minerals that have been remobilized and migrated to new sites of deposition by the influence of a temperature rise in the rocks.
2. The hydrothermal theory suggests that ore is deposited by mineralized, heated, aqueous solutions that have emanated from some igneous source. The volatile fluids would dissipate outwards and upwards to deposit ores as fissure filling or replacement ore bodies. This theory is not sufficient to explain certain ore deposits, such as the Mississippi Valley type and the Western Canadian ore bodies dealt with in this study since they have no obvious relation to igneous rocks.
3. The syngenetic theory suggests that ore deposits are formed concurrently with the host rock as a result of special environmental conditions bringing about sulfide precipitation at the site of sediment deposition on an ocean floor. Syngeneticists

invoke such an origin for the Rhodesian and Mansfeld copper deposits and have often attempted to explain the Mississippi Valley deposits on this basis. Some geologists explain the presence of metallic ions in the sea water as having come from sub-marine volcanic exhalations.

Origin of the Western Canadian Lead-Zinc Deposits

It has been established from the sulfur isotope data that the sulfur present as sulfide is not of magmatic origin. The heavy nature of the sulfur suggests another type of origin, possibly a biogenic one. The problem remaining is to find the source of the thousands of tons of metal which have gone into the production of the huge Pine Point deposit and the smaller Eldon, Kicking Horse, Monarch, and Hawk Creek deposits.

The absence of any obvious igneous source has been stressed. The closest igneous body in the Rocky Mountain area is the Ice River Complex, a syenitic assemblage of rocks consisting of jacupirangite, ijolite, nepheline syenite, and sodalite syenite phases (Campbell, 1961). The intrusive rocks cut the Middle Cambrian Ottertail formation and Goodsir Formation of Cambro-Ordovician age. A mica from the body yielded a potassium-argon date of 350 M.Y. (Baadsgaard et al. 1959). The complex lies roughly 18 miles south of the Monarch-Kicking Horse Mines and 17 miles west-northwest of the Hawk Creek deposit.

No igneous rocks younger than Precambrian are known to occur on the surface in the Pine Point area. An igneous, volcanic-like body, mentioned on page 47, has been discovered in the Imperial Steen River 12-19 well located at Lsd. 12 - Sec. 19, Rge. 121 - Twp. 21 W. 5 Mer. (lat. $59^{\circ} 31' 6''$ N; long. $117^{\circ} 51' 6''$ W). This well is about 150 miles southwest of the Pine Point mine. The only igneous rocks known to occur in the Beaver River area of northeastern British Columbia is the Beaver River syenite dyke (lat. $60^{\circ} 24'$ N, long. $125^{\circ} 47'$ W) which occurs 60 miles northeast of the Beaver River A-1 well. The Ice River Complex is 17 miles from the Monarch and Hawk Creek deposits. There appears to be no direct relationship between the ore bodies and

the igneous intrusions. The mineral orthoclase from this dyke yielded the age of 240 M.Y. (Baadsgaard et al. 1961).

A syngenetic origin of the ore deposits must also be ruled out since such an origin could not account for the vein-like Eldon and Hawk Creek deposits, the breccia-replacement deposits at the Kicking Horse-Monarch Mines or the massive lead-zinc ores in dolomite at Pine Point. Russell et al. (1960) have suggested that the lead and zinc in this type of deposit could have been incorporated into the sea as volcanic exhalations. He suggests that sulfates, and sulfur along with metallic halides could later be trapped in the volcanics and associated sediments only to be squeezed out by compaction and re-deposited at a later date. The absence of volcanic flow and tuff horizons in the stratigraphic section both in the Liard basin area and the Rocky Mountain region makes this kind of origin seem doubtful. The presence of a volcanic-like plug in the subsurface in the Steen River area, 150 miles southwest of the Pine Point mine, suggest there may have been volcanic activity occurring in the area in the late Paleozoic.

Brown (1965) has recognized the close isotopic resemblance of oceanic leads to normal ore lead of post Precambrian time. He found that the minimum range of 1.33 - 1.34 percent Pb^{204} in the oceanic lead corresponded almost exactly to values at which normal lead ores cease to exist on the continents. He thus postulates a genetic relationship of the two types of leads. Brown has put forth the suggestion that certain fluids containing lead, zinc, and other metal ions could exist as connate waters trapped in marine sediments. Lead is very scarce in sea water itself (less than .1 ppm) but may run as high as 40 ppm in recent marine sediments. The normal amount of lead in sedimentary rocks is 15 ppm or less.

The presence of anomalous leads in ore deposits always presents problems when lead isotope data is used to theorize on the origin of a deposit. Brown (1959) and others have suggested that radiogenic lead contamination could come from Precambrian basement rocks. This would require the ascent of contaminant bearing solutions from the basement; which might lie several hundred or several thousand feet

below the ore bearing sediments. Brown has estimated that one-fifteenth of the lead in the Mississippi Valley deposits would have had to come from the basement.

Brown (1959) reports lead from the Monarch mine as having an anomalous Pb^{204} value of 1.3 percent. If all of the Rocky Mountain leads are similarly anomalous then the contamination theory might apply here since contaminant bearing solution could easily have come from depth via the many thrust faults in the Rocky Mountain system. The only lead isotope data available on the Pine Point ore suggests that this lead lies on the borderline between anomalous and normal (Wilson et al. 1956).

The presence of connate water in sedimentary rocks is well established from oil well data although data on heavy metal content of these waters is scarce. Brown (1965) believes these metal bearing waters could at some time be subjected to heat from normal burial or perhaps an igneous source. The metals would be mobilized and concentrated if the right physico-chemical environment existed.

Noble (1963) discussed the water of compaction theory as the possible origin for the Colorado uranium deposit, the southwest U.S. red bed copper deposits, and the Mississippi Valley type lead-zinc deposits of the U.S. This theory becomes important when considering a connate water origin of the western Canadian low temperature lead-zinc deposits considered in this study.

Connate waters concentrated during compaction of sediments would be under pressures much greater than normal meteoric waters under hydrostatic pressure so these waters could be expected to move about through aquifers or they could remain in subsurface chamber until some driving force remobilized them. To acquire large volumes of metal in solution the connate waters would have to have solvent powers capable of leaching the metals from large volumes of rocks. The presence of lead and other metals in unusual quantities (40 ppm) in recent marine has been shown by Brown (1965). It is not impossible that these metals exist as soluble chlorides, carbonate, or bicarbonate complexes. Noble mentions the presence of lead, zinc and copper in active formation

waters in the Mississippi Valley region of the U.S. Even though these waters exist in a district rich in lead, zinc, and copper, the ability of waters to carry these elements is demonstrated. If a pressure or temperature differential was established in an area by a thermal or tectonic event these waters could be set in motion and sulfides could precipitate in an environment of lower pressure if the necessary agents of precipitation were available. The presence of hydrogen sulfide, derived from any number of sources, organic, biogenic, etc. would trigger precipitation of sulfide minerals.

Barton (1957) states that metals forming extremely insoluble sulfides, galena, sphalerite, etc. would have to be transported as complex ions or the tremendous volume of solution required to carry the sulfides would wash away the more soluble carbonates, sulfates, etc. associated with ore deposits. On the basis of calculations involving the activity in water of various anions that would combine with metals, he has tried to rule out the formation of soluble complex sulfides or hydrosulfides with metals other than those forming very stable complexes (mercury, arsenic, antimony, and perhaps gold and silver). What is needed is a solubility many times greater than the solubility indicated by the activity of the metallic ion or the sulfide. Barton feels that the formation of halide complexes might fulfil this requirement. Such a possibility should be considered in the origin of both the Rocky Mountain deposits and the Pine Point and Beaver River deposits. Although not true magmatic deposits, the ores probably should be classified as hydrothermal in the sense of being transported and deposited by a hydrous liquid medium. If the minimum temperatures obtained from the iron content of the sphalerites are accepted then the area must have been abnormally hot during the period of sphalerite formation.

Such a hydrothermal origin would account for the veins, bedded replacements, and breccia fillings characteristic of the ore deposits. Dolomitization such as that found at the Monarch-Kicking Horse, and Pine Point deposits, could be explained by hydrothermal solutions derived from a connate water or other source that had been heated up and remobilized by some heat producing event.

Ohle (1959) has implied a hydrothermal origin for the origin of the Mississippi Valley deposits in the United States. He admits a truly magmatic hydrothermal origin for these deposits poses problems which cannot be readily explained.

The connate water mechanism advocated by Brown (1965) might account for the Mississippi Valley type ores in Western Canada. In this case ore deposition would by no means be a rapid process. It would probably take 50 - 100 million years for the metals to concentrate in connate waters and would probably take another 10 - 20 million years to form a sizeable ore body when and if a heat source came into being. Time spans of this magnitude are not impossible when one considers the thickness of the sediments laid down in the Rocky Mountain region during Cambrian and Ordovician time, and those sediments deposited during Devonian time in the Liard basin.

Age of Mineralization

The exact age of ore deposition, in the Canadian Rocky Mountains in the Banff, Alberta, and Field, British Columbia areas, is not known. Since the ore deposits lie within Cambrian or Ordovician strata and are epigenetic, the deposits were emplaced after Cambrian and Ordovician time.

Some indication of the age of mineralization in the Eldon mine area is given by a potassium-argon age determination on the mineral sericite. The sericite was separated by hand and a potassium analysis was performed by the University of Alberta, Geology Department's rock analyst, Alex. Stelmach. H. Baadsgaard did the mass spectrometric analysis for radiogenic argon. The sample contained 6.22% K_2O (uncorrected for Rb_2O) and the argon was 97.9% radiogenic. The Ar^{40}/K^{40} ratio was equal to 0.01576 and the date was calculated on the basis of the constants: $\lambda_e = .589 \times 10^{-10}$ yr and $\lambda_\beta = 4.76 \times 10^{-10}$ yr. These values yielded a minimum age of 250 M.Y. Folinsbee, et al. (1963) determined the ages of bentonite horizons in the Exshaw Formation (Upper Devonian) in the Nordegg-Exshaw, Alberta area by dating sanidines using the K/Ar method. They obtained values ranging from 222 to 284

million years. These ages indicate the occurrence of some tectonic event prior to the Laramide Orogeny. The Laramide Orogeny, which occurred approximately 100-50 million years ago during Cretaceous and early Tertiary times, would probably up-date the sericite. The Eldon ores show signs of deformation (Plate III, No. 1, 2, 4), whether this deformation was caused by tectonism during the Laramide Orogeny is not known.

The age of the Pine Point and Beaver River mineralization is not known although it is fairly certain it was post-Devonian since the ores lie in Devonian strata. A galena from Pine Point yielded an age of 100-300 million years (Wilson, et al. 1956). Wilson, et al. (1956) report the lead isotopic ratio $206/204 = 18.4$ and 18.8 ; $208/204 = 38.6$ and 38.9 . These authors have indicated the ages of the two galenas to be 300 ± 300 M.Y. and 100 ± 300 M.Y. respectively. Although these leads appear to be normal the percent Pb^{204} is not indicated in the paper. The writer considers the validity of these results questionable until they are substantiated by future isotopic determinations on the Pine Point galenas.

PLATE I

PHOTOMICROGRAPHS OF THIN SECTIONS

- Figure 1. Sericite, intimately associated with galena, sphalerite, quartz and pyrite (Cubes). Eldon Mine-
x 10
- Figure 2. Twinned dolomite [(0221) as twin plane] along with sphalerite and galena (black). Hawk Creek -
x 10
- Figure 3. Zoned sphalerite in grey dolomite. Kicking Horse Mine-
x 10
- Figure 4. Same as Figure 3.
x 25
- Figure 5. Sphalerite replacing dolomite. Kicking Horse Mine-
x 10
- Figure 6. White, coarsely crystalline dolomite (grey) vein in grey fine grained dolomite. Quartz pod in centre of photo (white). Kicking Horse-
x 10
- Figure 7. Sphalerite (grey) in quartz (white) with pyrite cubes (black). Eldon Mine-
x 10
- Figure 8. Twinned sphalerite in quartz. Simple twins on (III) as composition plane. Eldon Mine-
x 10

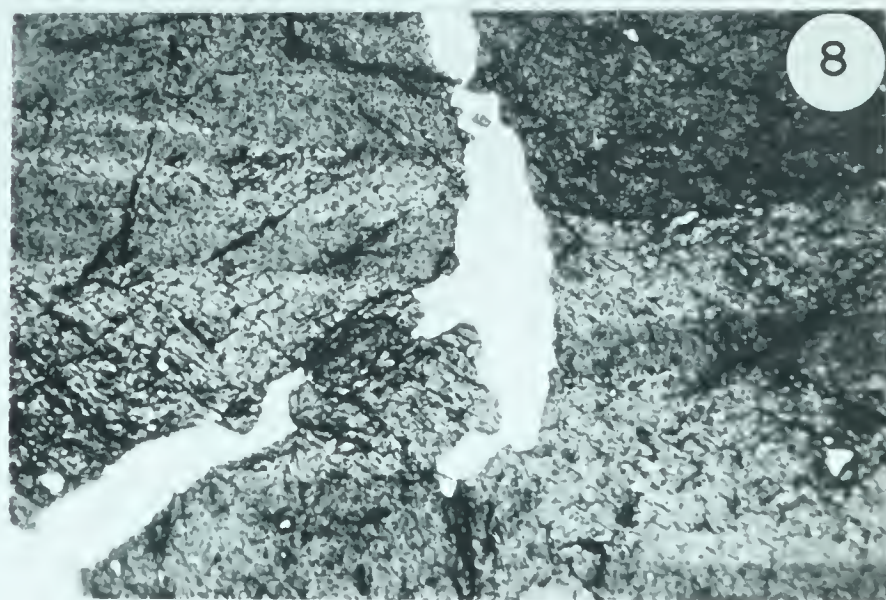
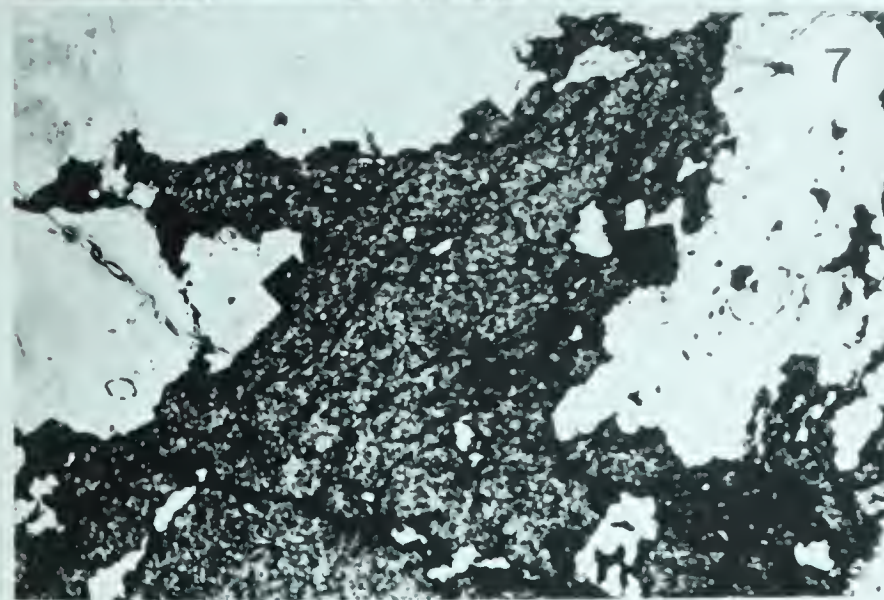
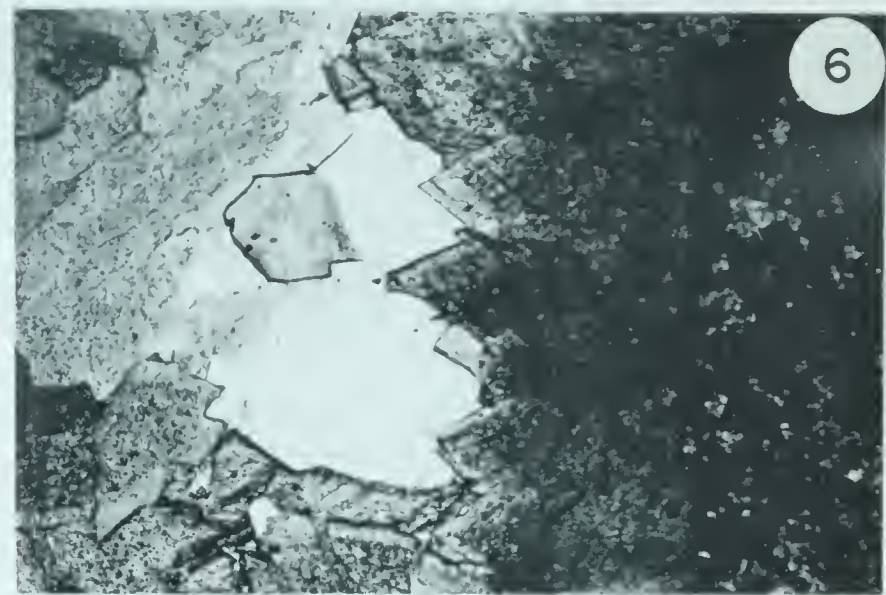
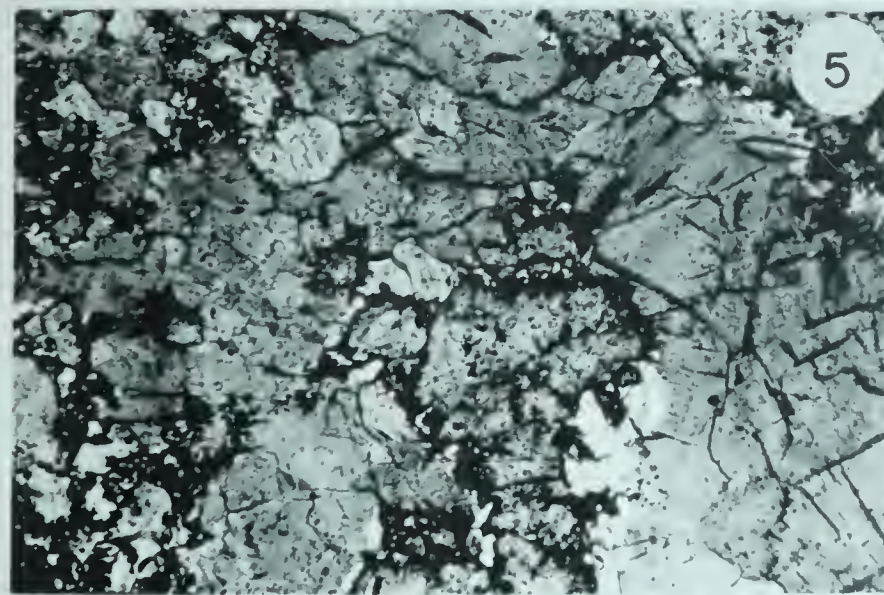
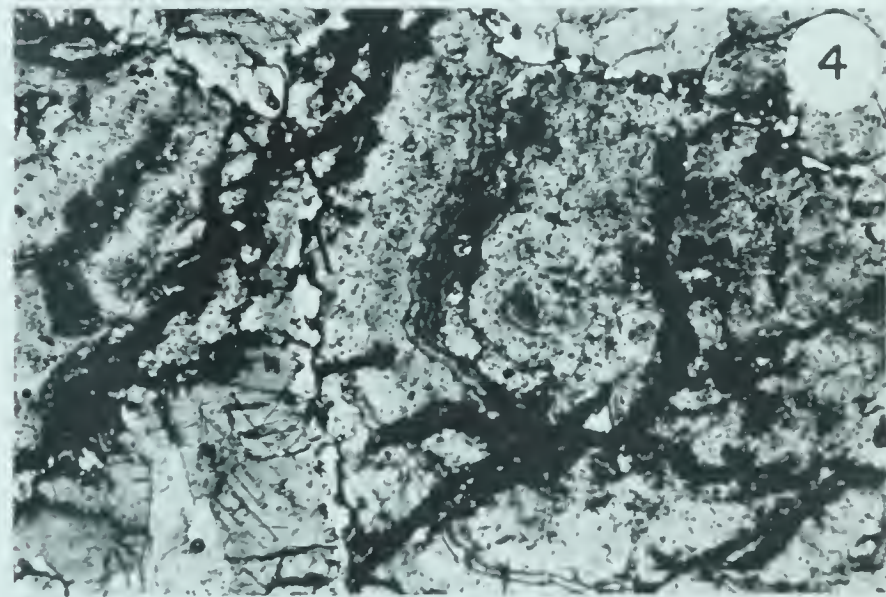
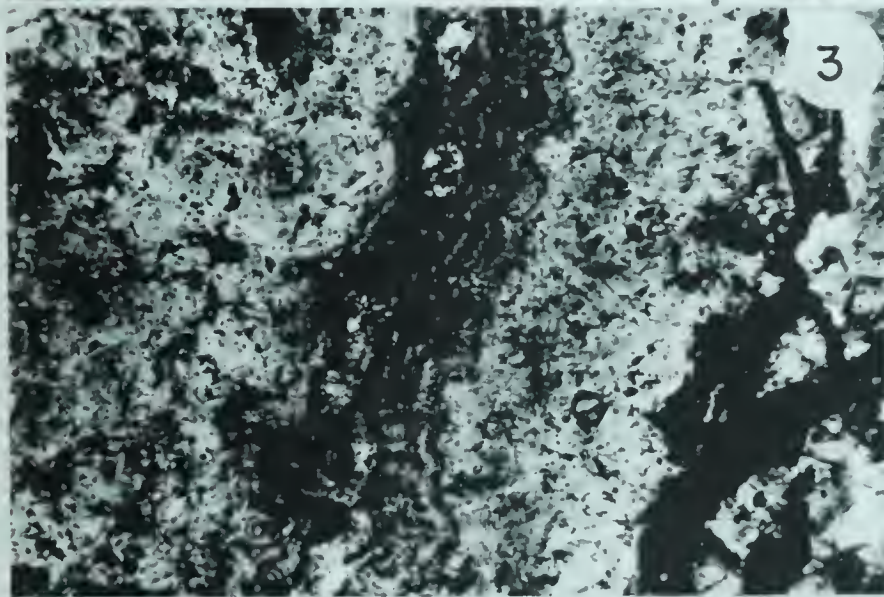
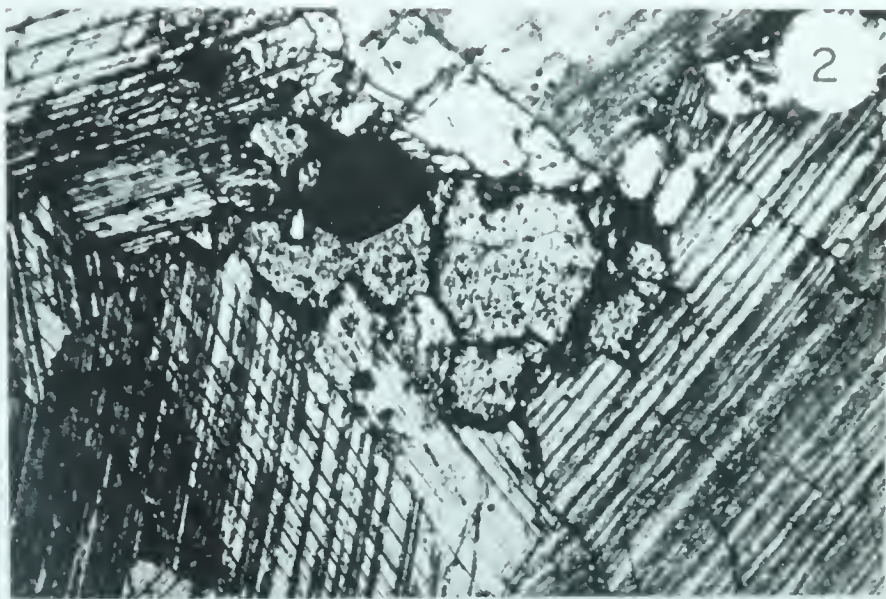
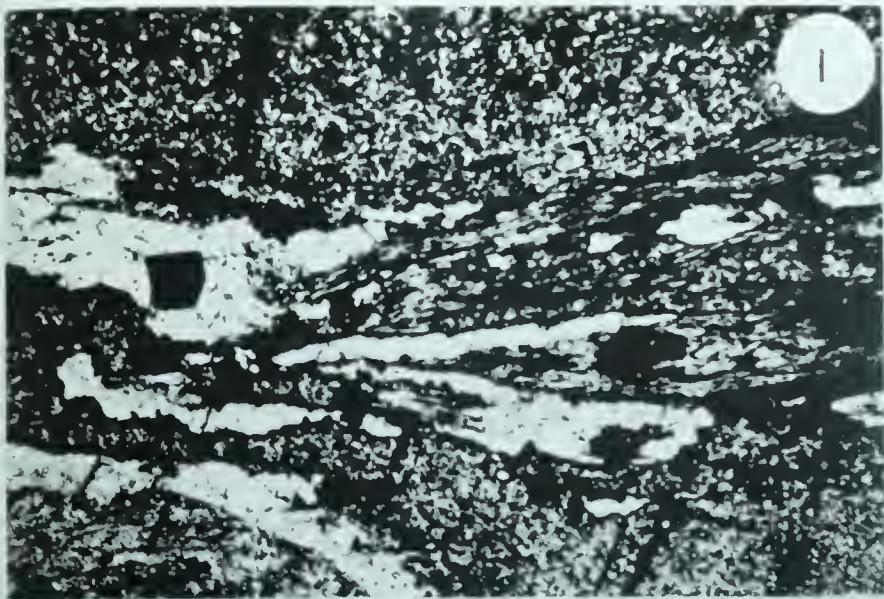


PLATE I.

PLATE II

PHOTOMICROGRAPHS OF POLISHED SECTIONS

- Figure 1. Galena (white) replacing sphalerite (light grey) in quartz (dark grey) gangue. Eldon Mine-
x 25
- Figure 2. Pyrite (white), galena (light grey), sphalerite (medium grey) in quartz gangue. Eldon Mine-
x 25
- Figure 3. Galena (white) replacing sphalerite (light grey) in quartz (dark grey). Eldon Mine-
x 25
- Figure 4. Chalcopyrite blebs (white) in sphalerite (grey) Eldon Mine-
x 64
- Figure 5. Paragenetic sequence of pyrite (white) sphalerite (medium grey), galena (light grey) in dolomite (dark grey). Hawk Creek-
x 10
- Figure 6. Paragenetic sequence of pyrite (white), sphalerite (medium grey), and galena (light grey). Hawk Creek-
x 25
- Figure 7. Galena (white) replacing dolomite on rhombohedral cleavage. Hawk Creek-
x 25
- Figure 8. Galena (white) replacing sphalerite (medium grey) in dolomite (dark grey). Note intimate association of the two minerals. Hawk Creek-
x 10

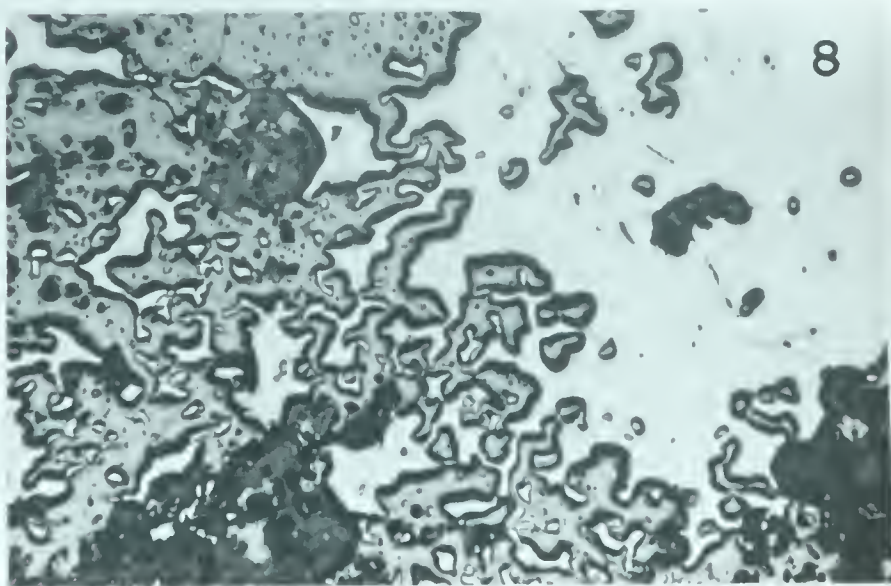
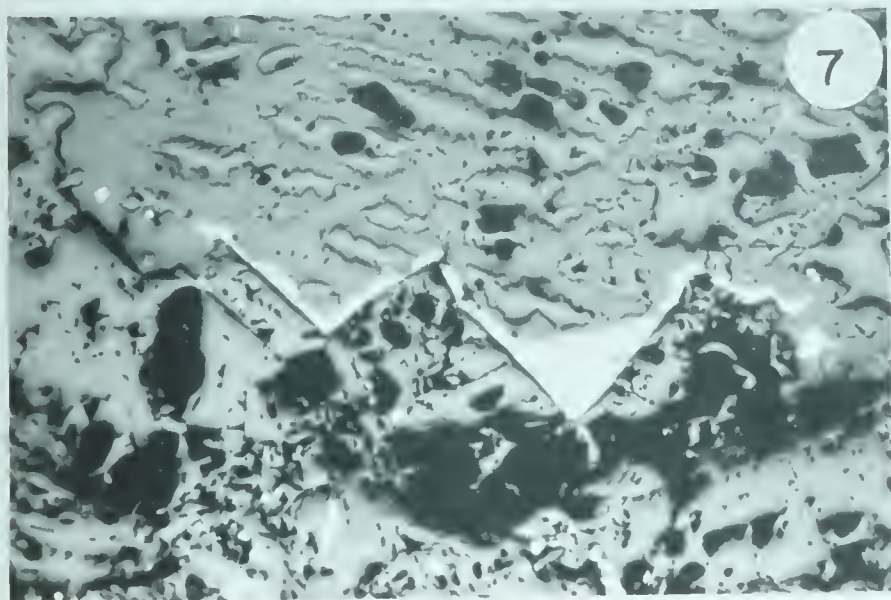
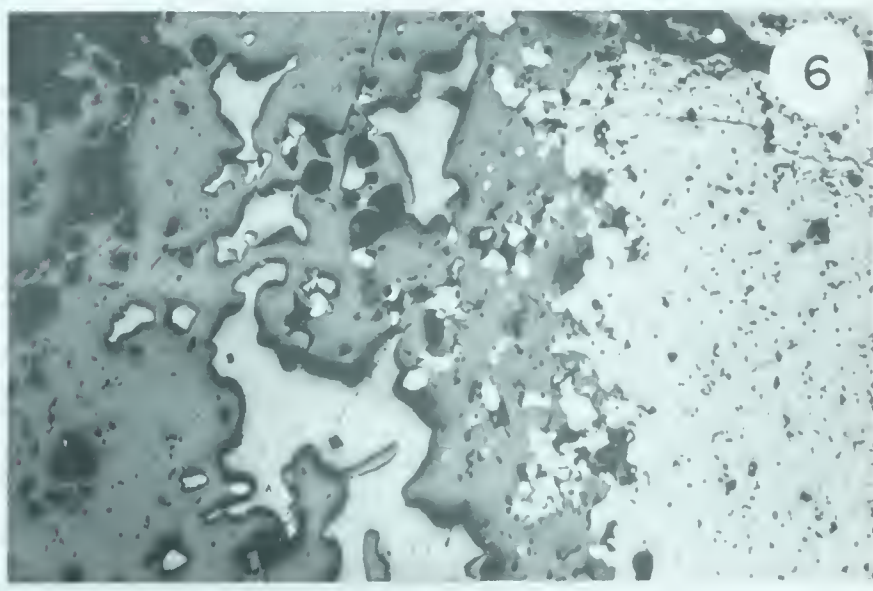
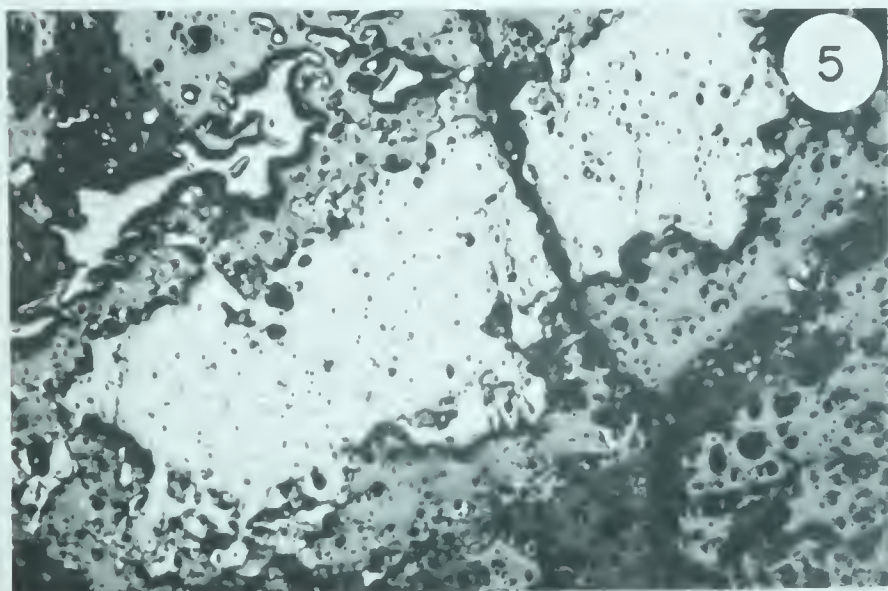
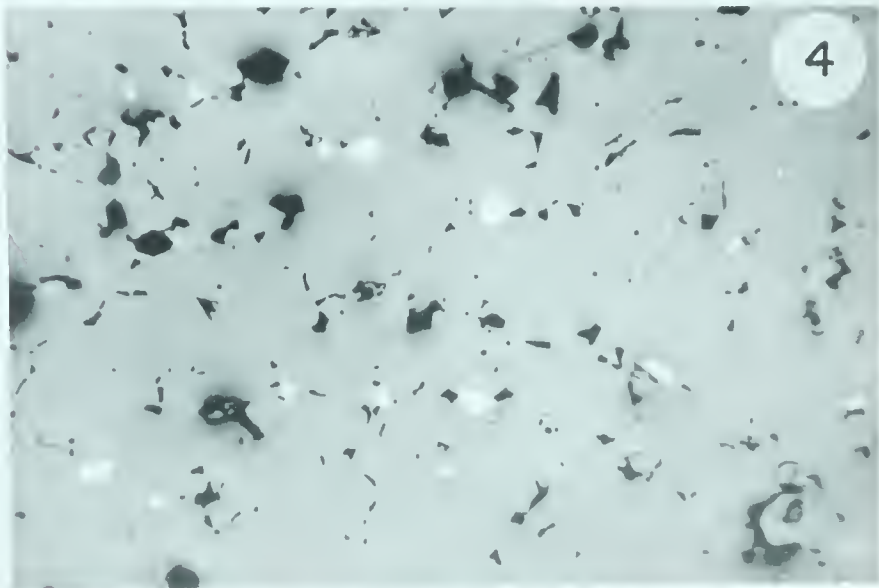
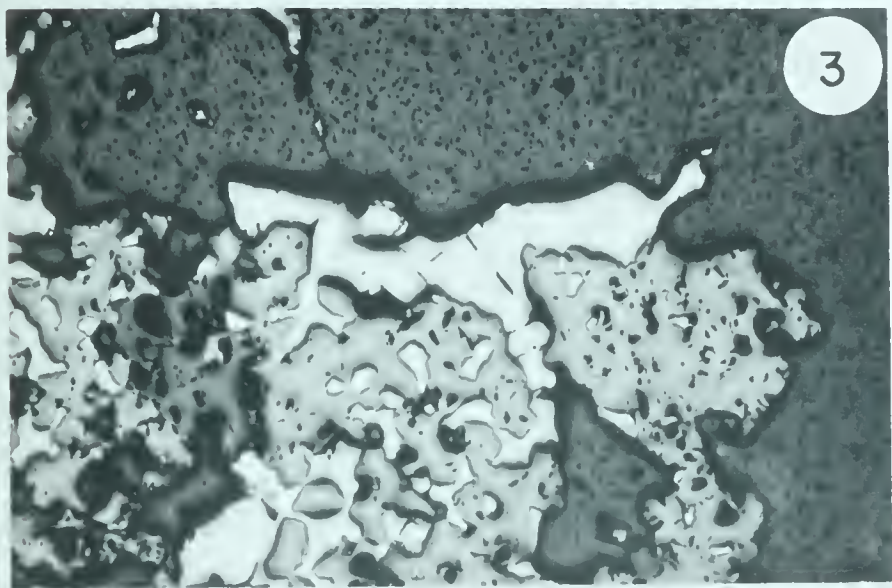
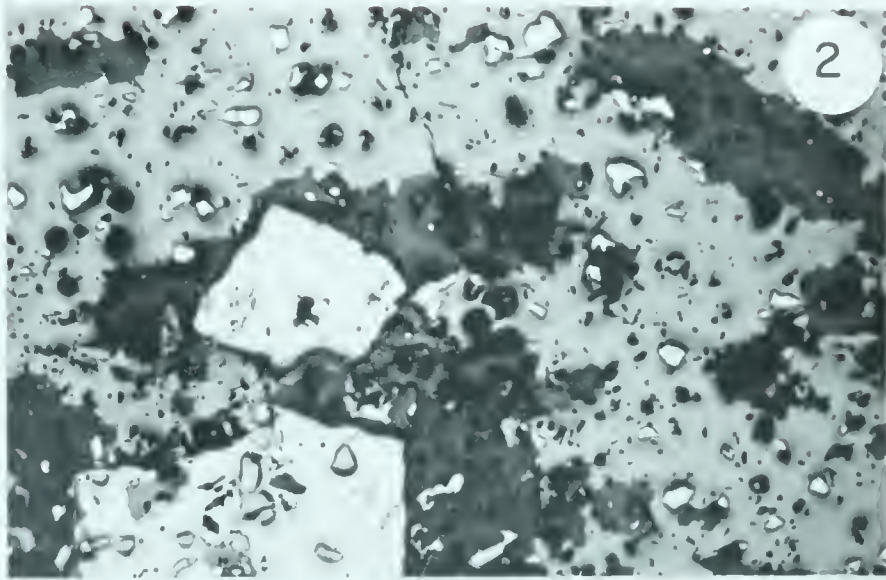
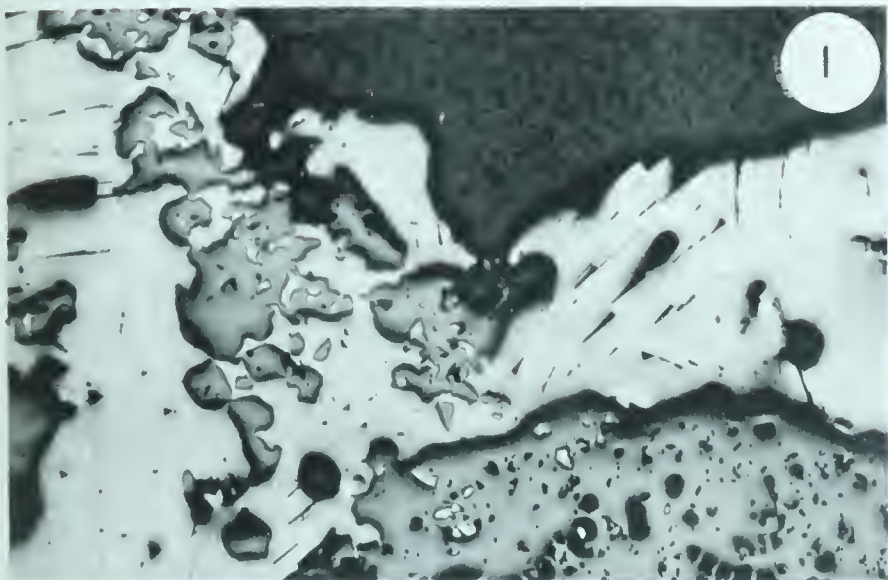
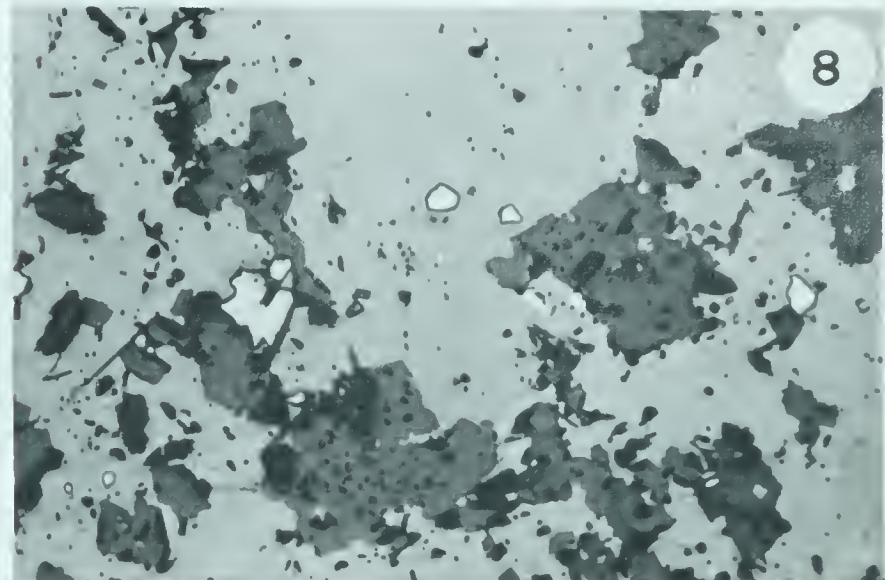
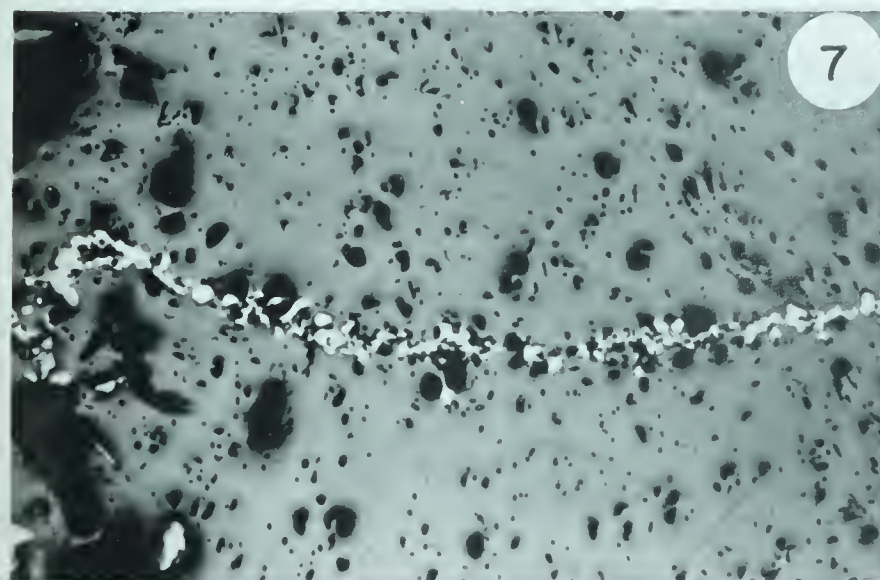
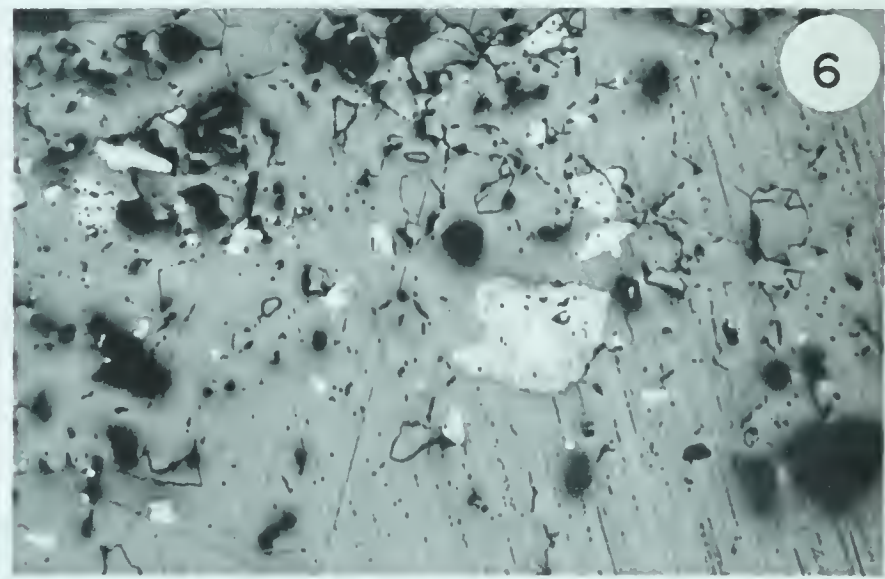
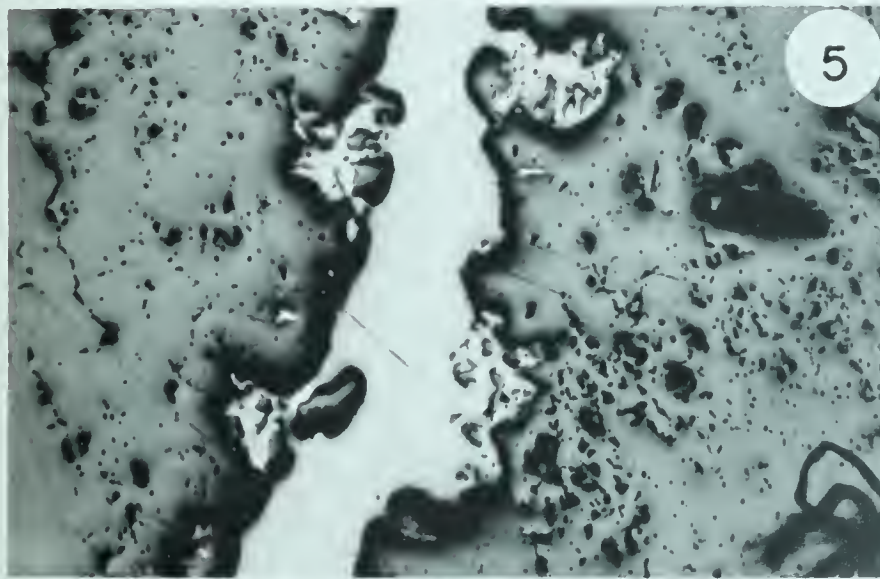
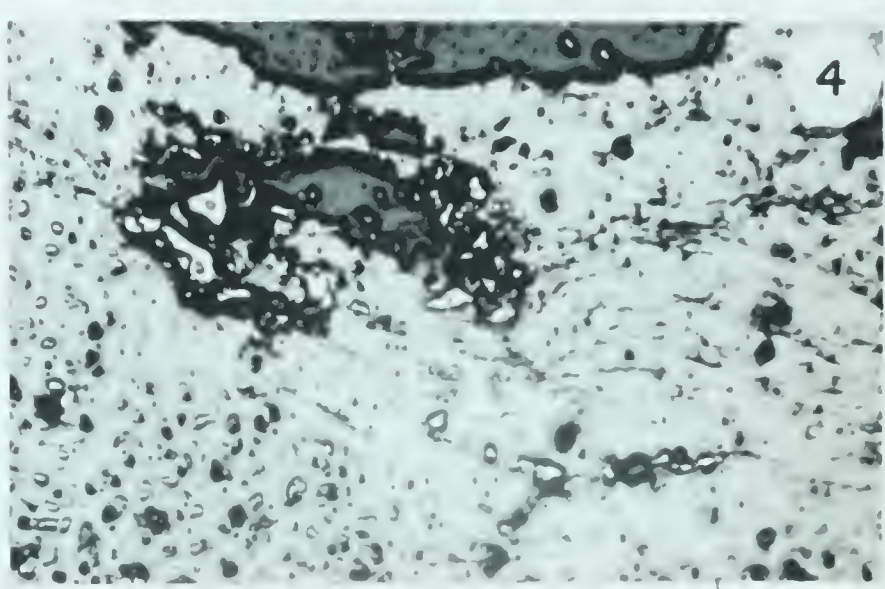
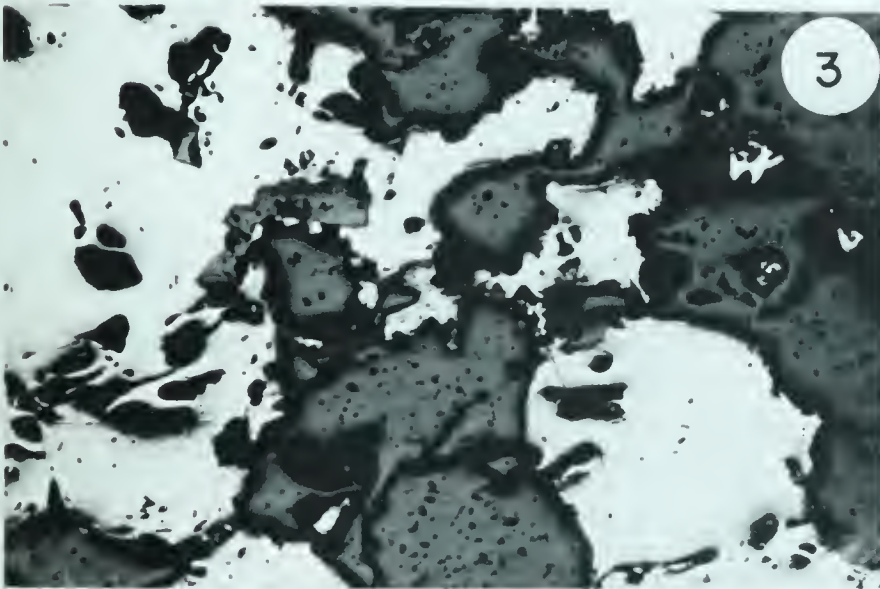
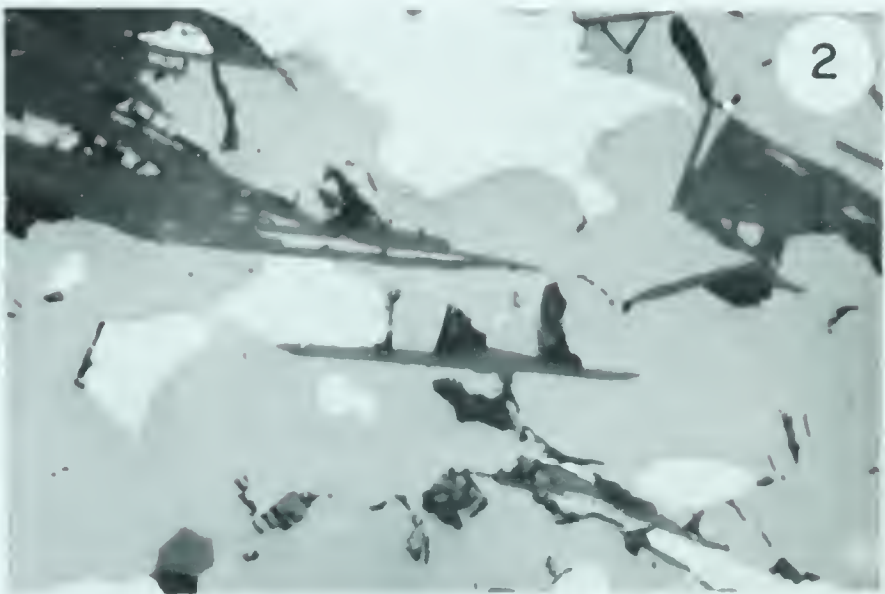


PLATE III

PHOTOMICROGRAPHS OF POLISHED SECTIONS

- Figure 1. Sphalerite (light grey) and galena (white) with orientated quartz prisms. Eldon Mine-
x 64
- Figure 2. Same as Figure 1.
x 160
- Figure 3. Chalcopyrite (white) in quartz gangue. Eldon Mine-
x 64
- Figure 4. Sphalerite (light grey), galena (white), in quartz (dark grey) gangue. Note fine quartz rods. Eldon Mine-
x 10
- Figure 5. Galena (white) band in sphalerite (grey). Pine Point-
x 25
- Figure 6. Pyrite (white) in sphalerite (grey). Sphalerite appears to be replacing pyrite. Pine Point-
x 25
- Figure 7. Pyrite (white) stringer in sphalerite. Hawk Creek-
x 25
- Figure 8. Sphalerite (light grey) and galena (white) in dolomite (dark grey). Kicking Horse Mine-
x 25



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APPENDIX I

PHYSICAL AND CHEMICAL TECHNIQUES

Sample Preparation

The samples obtained for use in the sulfur isotope analyses, the X-ray fluorescence analyses, and the powder photograph work were slabs with a rock saw and the different mineral species were drilled out of the slabs with a small diamond drill. The removal of the sulfides in this manner prevented the material from becoming contaminated with iron and other impurities from crushers that might have been used. The sulfide minerals were ground by hand in an agate mortar and stored in glass vials until used.

Powder Photograph Measurements

The powder photographs of 15 sphalerites were taken with a 114.6 mm standard camera on a Norelco power unit. The source of radiation was a cobalt tube that was energized by 25 KV and 15 MA, the emitted $\text{CoK}\alpha$ radiation was filtered through an iron filter.

The films were measured on a vernier graduated to .05 mm although estimations were made to .025 mm when possible.

X-ray Fluorescence

All samples prepared for X-ray fluorescence analysis were briquetted in an Applied Research Laboratories Inc. Briquetting machine type 4451, for 60 seconds at 15,000 p.s.i. Each sample was backed and rimmed with cellulose powder for strength. The diameter of the exposed sample was approximately 1/2 inch. Comparative X.R.F. studies were made using a sample of 1/2 diameter and a sample of standard diameter (1 inch). The emission in counts-per-second was observed to be 5 percent less in the smaller diameter sample. This difference is not thought to be critical unless extremely small amounts (50 ppm) of an element ore is present.

The samples were analyzed in Norelco-X-ray fluorescence equipment, the basic unit used was type 122 15/0. Radiation source was a Cr or Mo target tube energized by 50 K.V. and 40 M.A. A Lithium fluoride analyzing crystal was used in combination with a Scintillation counter operating at a detector voltage ranging from 810-880 volts, and a Flow Proportional Counter operating at 1460-1520 volts and receiving 0.25 S.C.F./H supply of 90% Methane, 10% Argon gas mixture. Complete recording conditions are given in Table 10.

The conversion from counts-per-second to weight percent was made with calibration curves set up with a number of prepared standards containing known percentages of the element being analyzed. No mass absorption corrections were necessary because the matrix in each sample (sphalerite or galena) is assumed to have similar absorption characteristics.

The precision error for each element was determined from the variation in counts-per-second of the sphalerite standard 105-2. The usual standard derivation function $(S.D. = \sqrt{\frac{(m - x)^2}{n - 1}})$ where m is mean value, x is a value and n is the number of values taken) was used and the precision expressed as a percent.

$$\frac{SD}{\text{mean}} \times 100$$

The estimation of detectability is made on the variation of the background of the standard and the detectability expressed as a percent. According to Spiegel (1961) ± 3 S.D. from the mean should include 99.17% of all points. Three times the S.D. of the background expressed as weight percent is the detectability. The statistics for all the elements are given in Table 11.

TABLE 10
RECORDING CONDITIONS FOR X-RAY FLUORESCENCE ANALYSES

<u>Element</u>	<u>Peak</u>	<u>B. G.</u>	<u>Xtal</u>	<u>CTR</u>	<u>Ctrv</u>	<u>X-rp</u>	<u>PH4</u>	<u>PHLV</u>	<u>PHWV</u>
Fe	57.50	55.50	Lif	Sc	820	Air	Int	1.5	0
Cd	15.06	14.00	Lif	Sc	850	Air	Int	1.5	0
Mn	63.00	64.50	Lif	F. P.	1460	Vac	Diff	11	6
S	45.15	46.00	E. D. D. T.	F. P.	1520	Vac	Diff	8	10
Se	31.68	32.50	Lif	Sc	850	Air	Int	1.5	0

ABBREVIATIONS

B. G.	Background
XTAL	Analyzing Crystal
CTR	Counter
CTRV	Counter Voltage
X-RP	X-ray Path
PHA	Pulse Height Analyzer
PHLV	Pulse Height Lever Voltage
PHWV	Pulse Height Width Voltage
LIF	Lithium Fluoride
E. D. D. T.	Ethylene-Diamine-d-Tartrate
F. P.	Flow Proportional Counter
Sc.	Scintillation Counter
Vac.	Vacuum
Diff.	Differential
Int.	Integral

TABLE 11
STATISTICS FOR X-RAY FLUORESCENCE

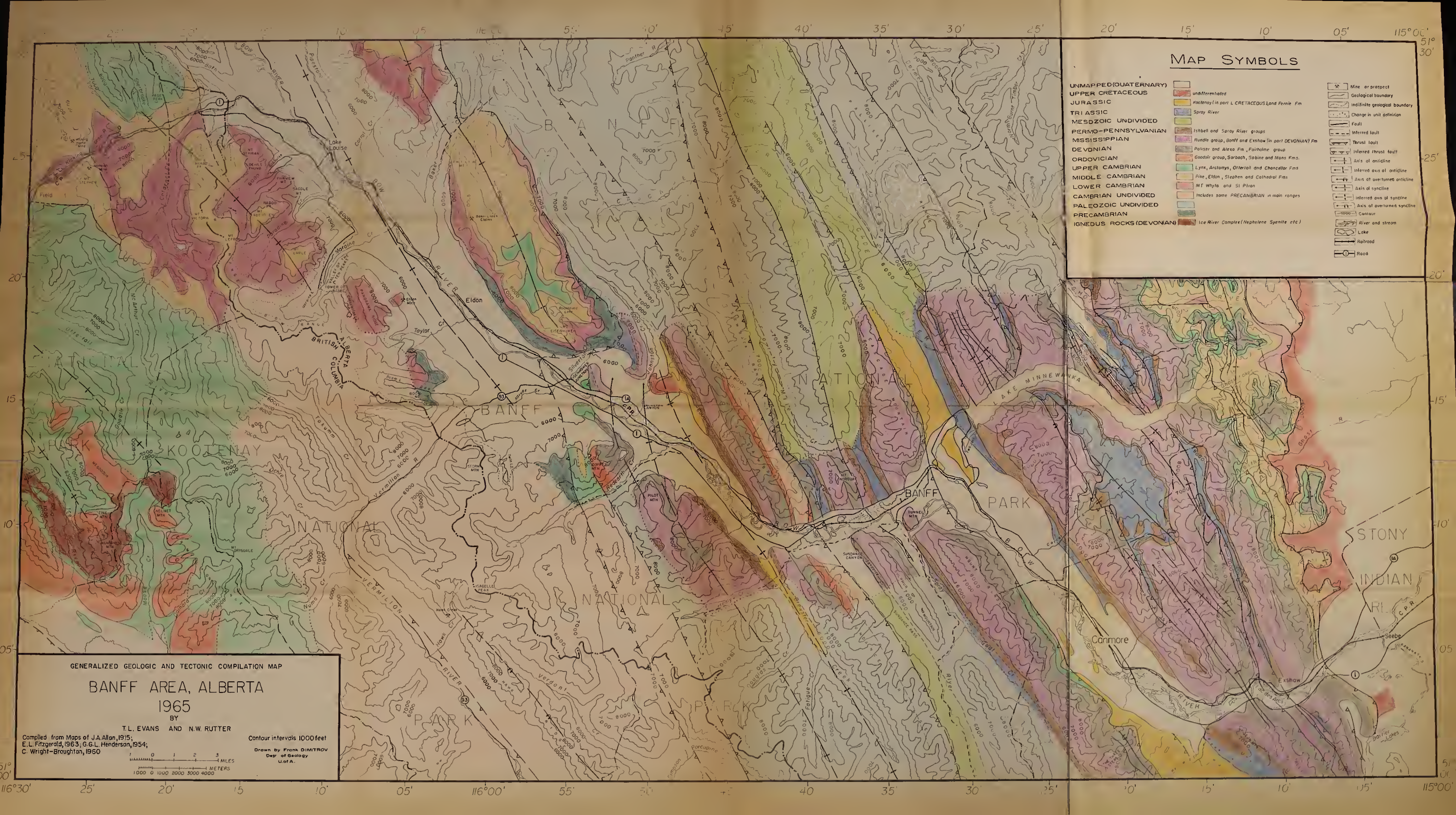
<u>Element</u>	<u>Precision %</u>	<u>Detectability (wt %)</u>
Fe	.30	.002
Cd	1.02	.007
Mn	.68	.002
S	1.34	.002
Se (ZnS)	6.2	.004
Se (PbS)	2.49	.005

APPENDIX II

PROPERTIES OF SPHALERITE

Name:	Zinc Blende, Black Jack (iron rich)
Formula:	ZnS - Pure
Optical:	Isotropic $N = 2.37 - 2.47$ (increases with iron)
Cleavage:	(110) Perfect
Hardness:	3.5 - 4.0
Color:	Colorless, Green, Yellow, Ruby Red, Brown to Black
Luster:	Non Metallic and Resinous to Submetallic; Adamantine
Streak:	White to Yellow and Brown
S.G.	3.9 - 4.1
Point Group:	$\bar{4}3m$
Space Group:	$F\bar{4}3m$
Cell Dimensions:	$a_o = 5.4093 - 5.4200$ (increases with iron, cadmium, and manganese).
Cell Content:	$Z = 4$





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